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CORRELATION OF ASH CONTENT OF WHEAT AND OF FLOUR¹

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Ash content of flour has been widely used as an index to flour grade. Numerous references appear in the literature concerning the relation of the two. Bailey (1925) has reviewed the early literature on this subject. As early as 1857 Mayer reported that the ash content of flour diminished with increasing refinement. Dempwolf (1869) noted the variable character of the ash of different wheats in a report showing the ash content of different grades of flour. Snyder (1904, 1905) called attention to the usefulness of ash content as a criterion of flour grade. Bailey (1913) found a positive correlation between percentage of ash and acidity, and a negative correlation between percentage of ash and color score of flour.

Flour mill chemists use the ash content of flour to a large extent in the control of grades. Flour is frequently sold with the maximum limit of ash content stipulated in the contract. Millers who employ chemical control tend to use the ash content of the flour produced as a standard by which milling practices are regulated.

While the ash content of flour has proved extremely useful in these respects, cereal chemists recognize the fact that there are limitations in the use of this factor as an absolute index to the percentage of extraction. Methods of conditioning and grinding vary to such an extent that the same wheat might yield flours of varying ash content if ground in different mills. Even with skillful supervision in a flour mill, there are slight fluctuations in the ash content of the flour from day to day,

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altho no noticeable change may be detected in the wheat blend going to the rolls.

It is common knowledge that different lots of wheat of the same market class vary in ash content. Berczeller and Wastl (1926, 1927) computed the coefficient of variability in several chemical constituents, including the percentage of protein, ash, fat, and cellulose in wheat. They found that the ash content was more variable than the protein content in two of the four wheat varieties studied. In the other two the protein content was somewhat more variable, but the ash content rated second in this particular, followed by the percentage of cellulose and of fat.

This was also the order of variability when they assembled, in a single calculation, the results of the analysis of 3878 samples distributed fairly uniformly through six crops. The modal value of ash content was 2.05%, which we assume to be calculated to a water-free basis. This is equivalent to 1.77% ash on a 13.5% moisture basis, which is approximately the median value of the modal class of our distribution of the 148 samples to which reference is made later in this paper.

Ash content of flour may be expected to vary with that of the wheat, providing variations in wheat ash are not occasioned primarily by differences in weight per bushel of the wheat. Bailey (1924) reported results of tests of four typical lots of spring wheat, showing that the ash content of the straight-grade flour increased with the increasing ash content of the wheat. Cereal chemists in the Pacific Coast states have indicated in conversations and correspondence that the wheats of that region are commonly high in ash and that the same is true of the flours milled from wheat grown in that region.

Records of the Minnesota State Testing Mill covering several years have shown substantial variations in ash content of the straight-grade flour that were generally assumed to be occasioned by corresponding variations in ash content of wheat. Reports of individual milling tests showing the ash content of each car-lot sample of wheat and the corresponding flour have been made by Sherwood (1925, 1926, 1928) in Bulletins 50, 54, and 62 of the State Testing Mill, covering the 1924, 1925, and 1926 wheat crops, respectively. Duplicate milling tests of 100-bushel samples were conducted in practically every instance.

A total of 148 wheat samples representing the 1924 and 1925 crops, and nearly all the samples of the 1926 crop were included in the study reported here. The results of the ash determinations, after correction to a uniform moisture basis, have been subjected to statistical analysis in order to establish whether or not the ash content of wheat was

correlated with that of straight-grade flour milled therefrom. A survey of the data recorded in these three State Testing Mill bulletins shows that the percentage of ash in wheat varied substantially in different samples of wheat grown in each of the crop seasons. Likewise average ash content of wheat varied from season to season.

The average ash content of wheat of the 1924 crop was practically the same as that of the 1926 crop, and the same was true of the average ash content of the flours of the two crops. The average ash content of both wheat and flour was higher for the 1925 crop, as shown by the data in Table I. The difference in the 1925 crop is significant and indicates that the ash content of the wheat of any particular crop, or of the wheat from a certain section of the wheat growing area, should be taken into account when setting ash standards for any grade of flour. If the standard in terms of ash content for a straight-grade flour as produced in these tests had been set arbitrarily at a fixed percentage, for example, 0.50%, the percentage of flour produced from wheat of the 1925 crop would have been substantially less than that of the other two years.

TABLE I
SUMMARY OF RESULTS FOR EACH OF THE CROP YEARS STUDIED

Crop year	No. of samples	Average weight per bushel lb.	Average yield of straight grade flour %	Average ash content of wheat, % \bar{x}	Average ash content of flour, % \bar{y}	Coefficient of correlation $r_{A_w A_s}$
1924	53	60.3	72.1	1.606	0.494	.73 \pm .04
1925	60	57.6	69.1	1.830	0.532	.80 \pm .03
1926	35	59.1	70.7	1.650	0.483	.80 \pm .04
1924-1926	148	58.9	70.6	1.696	0.507	.81 \pm .02

The coefficients of correlation (r) have been computed for each of the three years individually and for all tests of the three years taken collectively, and are recorded in Table I, together with other significant data. A high positive correlation is evident between the ash content of wheat (A_w) and of the straight-grade flour (A_s) of uniform extraction. This is true of each of the three crops, as well as of the three crops considered collectively.

During the course of these investigations the ash content was determined of 27 samples of the 1926 crop wheat as delivered to the first break roll, as well as the ash content of the same wheat before tempering and scouring. At the same time samples of the second middlings flour were taken for each determination. The authors recognize that in spite of all the care that could be exercised during the conditioning and the milling of wheat in these experiments, slight fluctuations in the ash content of the flour might result from conditions beyond the control

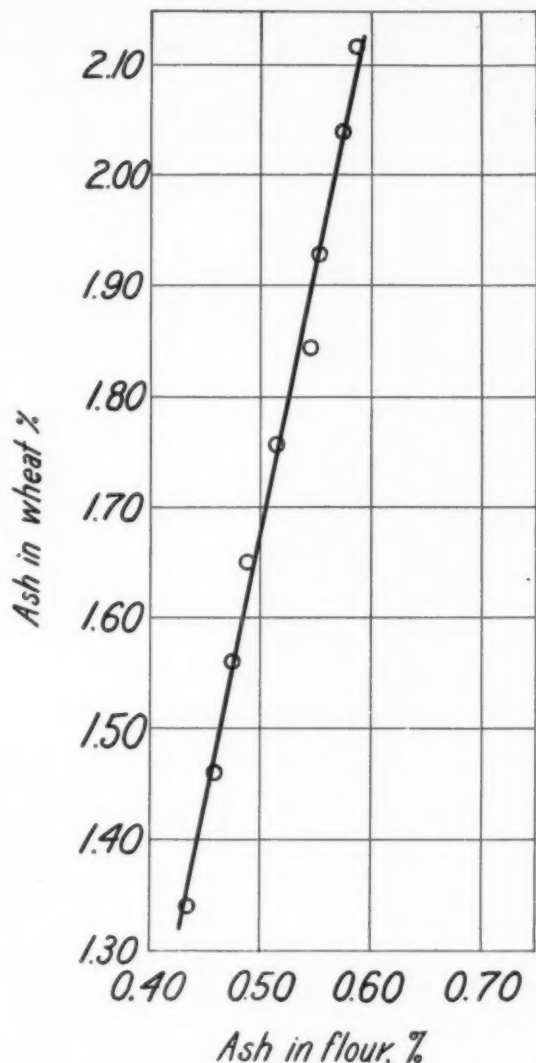
of the millers. It was believed that one of the best middlings flours would fairly represent the better portion of the endosperm of the wheat and serve as a further check in determining the relation between the ash content of wheat and of flour. For this purpose the second middlings flour was selected. Variations in ash content of this flour, when different wheats were milled, corresponded in general to the variations in the ash content of the wheat and of the straight-grade flour respectively. The ash content of the second middlings flours tested varied from 0.344% to 0.475%, the average being 0.395%. The average ash content of the straight-grade flours from the same wheat was found to be 0.495%.

Coefficient of correlation of the percentage of ash in wheat at the first break roll and the second middlings flour was found to be $r = 0.66 \pm 0.07$. That of the ash content of wheat at the break roll and the straight-grade flour for this series was found to be $r = 0.76 \pm 0.05$; and that of the ash of the second middlings flour and of the straight-grade flour, $r = 0.85 \pm 0.04$.

The high correlation of ash content of the second middlings stream and the straight-grade flour, which includes all the flour streams in this mill, indicates that the straight-grade flour constitutes as reliable an index to the character of the wheat in respect to ash content as one of the flour streams that represents a portion of the patent grade flour. The variation in ash content of the middlings flour is strong evidence that the endosperm of different wheats varies in ash content. With similar variations in the ash content of straight-grade flour, and in view of the high correlation between the ash content of these two flours, it cannot be assumed that the variations in ash content of the straight-grade flour are attributable to the conditions of milling or the influence of varying proportions of the low-grade flour streams comparatively high in ash content that make up a portion of the straight-grade flour. The conclusion is drawn that the variations in ash content of straight-grade flour milled from different wheats are due primarily to the ash content of these wheats.

In the data resulting from the determination of ash content of 148 samples of wheat, and the corresponding flours, the correlation ratio was found to be $+0.82$. This constitutes a measure of the relationship between two variables when this relationship is best described by a curve, which passes through the average of each column as the data are ordinarily segregated in a correlation table. When the correlation ratio is practically the same as the correlation coefficient, as in this instance, it

appears probable that the relationship between the two variables is essentially linear and is accordingly expressed by means of a straight line. Blakeman (1905) has suggested a criterion, or measure, of the linearity of regression by use of a formula that involves the relationship between



the correlation ratio and the correlation coefficient. This test of linearity was applied and the resulting value was 1.44. This is regarded by biometricians as indicating no substantial departure from a linear relationship in the data in question. The graph of the average of the values in each class serves to support the conclusion.

In addition to the computations expressed by means of correlation values, the same data were organized in a somewhat different manner. The wheat samples were grouped on a basis of their ash content and the mean percentage of ash in these wheats and in the flours milled from them was then calculated. The resulting values are shown in Table II, and are recorded graphically in the figure. The mean percentage of ash in the flour in each group was then divided by the mean

ash content of the wheat for the same group, or, as expressed in the table, A_f/A_w . The resulting values are recorded in the right hand column of the same table. From these data it appears that the ratio of

ash in the flour to ash in the wheat changes in progressing from the low-ash to the high-ash wheats. There was only one exception to this sequence, that was the wheat containing from 1.800% to 1.899% of ash.

TABLE II
AVERAGE OF ASH CONTENT OF WHEAT AND OF STRAIGHT-GRADE FLOUR
ARRANGED ON THE BASIS OF THE PERCENTAGE OF ASH IN THE WHEAT

Ash content of wheat by groups, per cent		Average ash content of flour in group, per cent	
Range	\bar{A}_w	\bar{A}_s	\bar{A}_s / \bar{A}_w
1.300-1.399	1.341	0.434	0.324
1.400-1.499	1.460	.459	.314
1.500-1.599	1.560	.475	.304
1.600-1.699	1.649	.488	.296
1.700-1.799	1.755	.514	.293
1.800-1.899	1.843	.545	.296
1.900-1.999	1.928	.553	.287
2.000-2.099	2.041	.573	.281
2.100-2.199	2.118	0.584	0.276

From the values given in Table II it appears that the factor to be used in estimating the ash content of straight-grade flour from the ash content of the wheat accordingly must be varied with the percentage of ash in the wheat. This factor will be lowered as the ash content of the wheat increases. In the mill in which these wheat samples were ground the factor was of the order of 0.30, with wheats containing 1.60% of ash, and 0.28 with wheats containing 2.05% of ash. This difference in the factor is not large, nevertheless it is large enough to justify its inclusion in a formula devised for estimating the percentage of ash in flour of any percentage of extraction from the ash content of the wheat.

The question may be raised as to whether or not the variations in the ash content of wheat were the consequence of or related to the relative plumpness of the grain or the weight per bushel. To answer this question the coefficient of correlation of weight per bushel of the wheat (W) and the ash content of the wheat (A_w) was computed. The resulting value, $r = -0.46 \pm 0.04$, indicates that in approximately half the instances these two characteristics are negatively correlated. This might be anticipated, perhaps, in view of the fact that the normal wheat pericarp contains more ash than the endosperm (in percentage) and that light wheats have less endosperm (in percentage) than heavy wheats.

When the correlation between weight of wheat per bushel and ash in flour was computed, the resulting coefficient was $r = -0.32 \pm 0.05$,

which is significantly lower than the coefficient of correlation of weight per bushel and ash in wheat.

The method of partial correlation was then resorted to, in an effort to estimate the correlation of ash in wheat and in flour with weight per bushel held constant. The resulting value $w^{r_{A_w A_s}} = +0.78$. This is of the same order of magnitude as the simple correlation coefficient $r_{A_w A_s} = +0.81$, and adds further confirmation to our assumption that the ash content of the wheat will be reflected in that of the flour.

To test this assumption further, the data resulting from analysis of thin wheats weighing less than 57 pounds per bushel, and the unusually plump wheats weighing more than 61 pounds per bushel were separated from the other data. The latter, representing 114 samples, were then subjected to the computation of the coefficient of correlation of ash in wheat and in flour. In this limited group the range in weight per bushel was not large, and none of the samples were sufficiently shrunken to occasion any difficulty in milling. The value $r_{A_w A_s} = 0.76 \pm 0.03$ is again approximately the same as the corresponding value when all wheats were used. Thus it appears that when the ash content of wheats of the same degree of plumpness varies, that of the flour is likely to vary in the same direction.

Summary

Ash content of straight-grade flour was found to be positively correlated with the ash content of the wheat from which the flour was milled in 148 samples of wheat representing three crops. Coefficient of correlation of these two variables, $r = +0.81 \pm 0.02$, is of sufficient magnitude to indicate that a relatively small proportion of the samples failed to correspond to the relationship that has been observed.

The correlation ratio in the instance of the same variables, $\eta = +0.82$, is so nearly the same as the correlation coefficient as to justify the conclusion that the ratio between the two variables is essentially linear. This conclusion is supported by the calculation of Blakeman's criterion of linearity.

When a selected group of wheat samples was taken that represented all the wheats weighing more than 57 and less than 61.1 pounds per bushel, the correlation coefficient of ash in wheat with ash in flour was $r = +0.76 \pm 0.03$. This differs so little from the corresponding value of r resulting from the inclusion of all the wheat samples as to indicate that variations in weight per bushel occasioned no variations in the relation between ash content of wheat and ash content of flour.

Partial correlation of ash content of all the wheat samples and ash content of flour was next computed, with weight per bushel held constant. The resulting value $w^{r_{A_w A_b}} = +0.78$, which again is nearly identical with the coefficient of correlation r determined in the two instances detailed above, further supports the assumption that the ash content of the endosperm varies with the ash content of the entire kernel.

Ash content of a highly refined middlings flour was correlated with ash content of the wheat in the same degree as was that of the straight-grade flour.

It accordingly appears that the percentage of ash in a flour cannot be used as a measure of the percentage extraction of that flour unless something is known concerning the ash content of the wheat from which the flour is produced.

Literature Cited

- Bailey, C. H.
1913 Relation of the composition of flour to baking quality. *Can. Miller and Cerealists*, 5: 208-209.
1924 Report of operation, State Testing Mill. *Minn. State Dept. Agr., Bull.* 34.
1925 The chemistry of wheat flour. The Chemical Catalog Company. New York.
- Berczeller, L., and Wastl, H.
1926 Ernährungsslehre und Variations-statistik. I. *Biochem. Z.* 177: 168-180.
1927 Ernährungsslehre und Variations-statistik. IV. *Biochem. Z.* 181: 117-132.
- Blakeman, J.
1905 On tests for linearity of regression in frequency-distributions. *Biometrika*, 4: 332.
- Dempwolf, O.
1869 "Untersuchung der Ungarischen Weizens und Weizenmehls." *Ann. Chem. Pharm.*, 149: 343-350.
- Mayer, W.
1857 "Untersuchung der vorzuglichsten Cerealien aus den Provinzen Bayerns zunächst auf ihren Gehalt an Phosphorsäure und Stickstoff." *Ergibnisse lands. und agr.-chemie Versuche*, Heft I, 1-45.
- Sherwood, R. C.
1925 Report of operation, State Testing Mill. *Minn. State Dept. Agr. Bull.* 50.
1926 Report of operation, State Testing Mill. *Minn. State Dept. Agr., Bull.* 54.
1928 Report of operation, State Testing Mill. *Minn. State Dept. Agr., Bull.* 62.
- Snyder, H.
1904 Wheat and flour investigations. *Minn. Agr. Expt. Sta. Bull.* 85 (Note p. 191).
1905 Testing wheat flour for commercial purposes. *J. Am. Chem. Soc.* 27: 1068-1074.

DETERMINATION OF HYDROGEN-ION CONCENTRATION OF FLOUR-WATER MIXTURES

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Two methods for the determination of hydrogen-ion concentration of flour-water mixtures have been employed in the writers' laboratories, viz., the colorimetric and the electrometric methods. With the latter method both hydrogen and quinhydrone electrodes have been used.

The Colorimetric Method

The colorimetric method is often recommended on the score of quickness of working. Probably, however, the initial cost and elaboration of the necessary electrometric apparatus are the real difficulties, for the saving of time attributed to the colorimetric method is largely imaginary. A large number of standard buffer solutions have to be made up at intervals and these require the making of carefully standardised solutions of sodium hydroxide, acid potassium phthalate, and acid potassium phosphate. Fresh colour standards made by mixing indicators with standard buffer solutions have to be made at frequent intervals, owing to the fading of the colours even if kept in the dark. Against this the electrometric method, once the apparatus has been set up, requires the making up of only one or two buffer solutions on which check determinations can be made from day to day as tests of the electrodes and of the proper functioning of the other parts of the apparatus. In both colorimetric and electrometric methods, filtered or centrifuged extracts of flour have to be made and this is the most lengthy part of the determination of H-ion concentration. In the determination of the H-ion concentration of bread, scones, etc., by dropping the indicator on the article itself, only approximate results can be obtained and sometimes these are misleading, owing to the actual change in colour of the indicator in contact with the solid scone or bread. On the score of accuracy there is no comparison between the two methods, and consequently there is very little indeed to recommend the use of colorimetric methods in the determination of the H-ion concentration of flour extracts.

Certainly such methods cannot be regarded as methods of precision for such purposes, as can be seen by the data given in Table I. To samples of a filtered flour extract, varying amounts of acid and alkali were added so as to obtain samples of flour extracts ranging in H-ion concentration from pH 5 to 7. These concentrations were determined colorimetrically and electrometrically using the quinhydrone electrode in the manner described later, and the results are given in Table I.

TABLE I
COMPARISON OF H-ION CONCENTRATIONS OBTAINED COLORIMETRICALLY AND ELECTROMETRICALLY

pH			pH	
A Quinhydrone electrode	B Methyl red	Difference A-B	C	Difference A-C
4.96	5.05	-.10
5.16	5.25	-.09
5.52	5.55	-.03
5.69	5.70	-.01
5.95	5.90	+.05
6.16	6.10	+.06
	Brom cresol purple		Brom thymol blue	
6.16	5.95	+.21	< 6.0	> +.16
6.35	> 6.20	< +.15	6.1	+.25
6.48	6.50	-.02	< 6.3	> +.18
6.70	> 6.70	+.00	6.5	+.20
6.77	> 7.00	-.23	< 6.7	> +.07
6.93	< 7.0	> -.07
	Chlor phenol red			
5.04	5.10	-.06
5.24	5.25	-.01
5.49	5.50	-.01
5.70	5.70	.00
5.88	5.90	-.02
6.11	6.05	+.06

The results obtained by the two methods in the pH region of 6 to 5 showed good agreement, while those in the region of pH 6 to 7 showed large differences.

The H-ion concentrations of the filtered extracts of six different flours were determined by the quinhydrone electrode and colorimetrically, using chlor phenol red. The results are given in Table II and show significant differences.

The H-ion concentrations of six loaves were determined by dropping methyl red on cut slices. All six loaves were judged to have a H-ion concentration equal to pH of 5.5 with no apparent differences between them. The H-ion concentrations were then determined by the quinhydrone electrode and found to be equal to pH 5.60, 5.64, 5.54, 5.64, 5.56, 5.65.

TABLE II
COMPARISON OF H-ION CONCENTRATIONS OF DIFFERENT FLOURS OBTAINED
COLORIMETRICALLY AND ELECTROMETRICALLY

Flour No.	Quinhydrone	Chlor phenol red	Difference
S 72	6.06	5.95	— .11
S 79	6.17	6.10	— .07
S 80	6.19	6.10	— .09
S 84	6.33	6.15	— .17
S 95	6.28	6.20	— .08
S 96	6.22	6.25	+ .03

Four scones were made from a self-raising flour containing varying ratios of acid calcium phosphate and sodium bicarbonate. The H-ion concentrations were determined by dropping various indicators on cut slices of the scones and also electrometrically. The results given in Table III are widely discordant. It should, however, be pointed out that the H-ion concentration of a loaf, or a dough, or a scone is not necessarily the same in all parts of the article and these local differences may quite well be a main factor in producing the wide differences observed between the different indicators.

TABLE III
H-ION CONCENTRATIONS OF SCONES EXPRESSED AS PH DETERMINED COLORIMETRICALLY
AND ELECTROMETRICALLY

Scone No.	Quinhydrone	Methyl red	Brom cresol purple	Brom thymol blue	Thymol blue
1	7.96	...	7.0	7.4	8.0
2	7.46	...	6.6	6.4	...
3	6.79	6.0	6.0	< 6.0	...
4	6.48	5.6	5.8	< 6.0	...

The Electrometric Method

Hydrogen electrode.—The hydrogen electrode was used for some time with completely satisfactory results. The electrode used was of the modified Bunker type. It can be easily and cheaply made by an inexperienced glass blower. The actual electrode consists only of a short piece of platinum wire projecting through the sealed end of a glass tube, and consequently a number of these can be quickly platinised and kept under water saturated with hydrogen. These electrodes give entire satisfaction. The other parts of the apparatus were made by the Cambridge Instrument Company and consisted of a slide wire potentiometer, A.M. mirror galvanometer with lamp and scale, Weston standard cell, calomel half cell, and necessary accumulators. The apparatus is sensitive to 0.1 m. volt (=0.002 pH) but readings of pH obtained by interpolation from the curve are usually taken to the nearest 0.01.

When using the hydrogen or the quinhydrone electrode the H-ion concentration of a buffer solution of known pH was always first determined, as this acted as a check on the correct working of the electrodes and of the other parts of the apparatus.

Quinhydrone electrode. — Subsequently we set up a quinhydrone electrode using the following chain as recommended by Biilmann (1924):

Pt.	Flour+water + quinhydrone	saturated KCl	0.01 N HCl + 0.09 N KCl + quinhydrone	Pt.
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A series of determinations of pH of a number of flour-water mixtures carried out by the hydrogen and the quinhydrone electrodes gave excellent agreement, as shown by the results collected in Table IV. After the electrodes had been in use for a few days, however, very discordant results were obtained, as shown in Table V. In all cases the pH observed with the quinhydrone electrode was smaller than that obtained by the hydrogen electrode. This difference increased with time, owing to a drift in the direction of increasing acidity that was observed with the quinhydrone electrode. For example, the apparent H-ion concentration of a flour-water extract after 1 minute from adding quinhydrone = pH 6.12. That after 30, 60, 90, and 120 minutes was pH 6.07, 5.98, 5.92, and 5.89, respectively.

No such drift occurred with the hydrogen electrode.

TABLE IV
H-ION CONCENTRATIONS OF VARIOUS FLOURS DETERMINED BY HYDROGEN AND QUINHYDRONE ELECTRODES: SHOWING INITIAL AGREEMENT BETWEEN THE TWO METHODS

Flour No.	pH as determined by use of		Difference
	Hydrogen	Quinhydrone	
Q 101	6.26	6.25	— .01
Q 102	6.35	6.34	— .01
Q 103	6.78	6.76	— .02
Q 104	6.46	6.47	+ .01
Q 105	6.40	6.44	+ .04
Q 106	6.40	6.38	— .02

Cleaning the platinum electrodes either by heating in an alcohol flame or by boiling in aqua regia did not remove the trouble. Heating in an alcohol flame caused a drift in the opposite direction, i.e., in the direction of decreasing acidity, which only disappeared after several hours. For example, the apparent H-ion concentration of a buffer solution immediately after heating and cooling the electrode

= pH 5.41. That after 15, 30, and 60 minutes, and 3 hours was pH 5.47, 5.51, 5.53, and 5.56, respectively.

TABLE V
H-ION CONCENTRATIONS OF VARIOUS FLOURS DETERMINED BY HYDROGEN AND QUINHYDRONE
ELECTRODES: SHOWING SUBSEQUENT DISAGREEMENT BETWEEN THE TWO METHODS

Flour No.	pH as determined by use of		Difference
	Hydrogen	Quinhydrone	
Q 107	6.54	6.40	— .14
Q 108	6.37	5.92	— .45
Q 109	6.26	5.95	— .31
Q 110	5.60	5.48	— .12
Q 111	6.44	6.19	— .25
Q 112	6.36	6.31	— .05
Q 113	6.17	6.03	— .14
Q 114	6.27	6.02	— .25
Q 115	6.39	6.18	— .21
Q 116	6.21	6.09	— .12
Q 117	6.17	5.97	— .20

Gold electrodes were then tried with completely satisfactory results, as Table VI shows. Determinations of H-ion concentration carried out on different days on the decantates from 100 samples of the same flour by means of the quinhydrone electrode gave results, expressed as pH, between 6.09 and 6.16. These results fell on a normal distribution curve, the mean value being 6.12. The probable error was ± 0.01 . The variability of results obtained by the quinhydrone electrode appears to be greater than that by the hydrogen electrode, although we have not determined the probable error of the latter. It will be seen from Table VI that the differences between the pH's determined by the two electrodes fall within the range of 3 times the probable error of the quinhydrone electrode. These differences are therefore not significant.

Gold electrodes have continued to give satisfactory results during the last two years. They do not appear to become poisoned and do not even appear to need cleaning other than by washing well with water. After several weeks use they have given the same pH for a standard buffer solution before and after cleaning by heating in the alcohol flame. Occasional check determinations against the hydrogen electrode have shown excellent agreement between the two methods. Subsequently a saturated calomel half cell was substituted for the quinhydrone half cell. All determinations were carried out at 25°C.

TABLE VI
H-ION CONCENTRATION OF VARIOUS FLOURS DETERMINED BY HYDROGEN AND QUINHYDRONE
ELECTRODES (USING GOLD INSTEAD OF PLATINUM): SHOWING AGREEMENT
BETWEEN THE TWO METHODS

Flour No.	H-ion concentration of flour extracts as determined by use of		
	Hydrogen	Quinhydrone	Difference
Q 118	pH = 6.35	pH = 6.37	+ .02
Q 119	6.14	6.13	— .01
Q 120	6.05	6.08	+ .03
Q 121	4.90	4.91	+ .01
Q 122	5.48	5.49	+ .01
Q 123	6.13	6.14	+ .01
Q 124	6.19	6.21	+ .02
Q 125	6.28	6.26	— .02
Q 126	6.24	6.21	— .03
Q 127	6.25	6.25	.00
Q 128	6.14	6.16	+ .02

This 'poisoning' of the bright platinum electrodes in the 'quinhydrone electrode' is so striking a phenomenon, causing as it does such relatively enormous errors in the determination of H-ion concentration by this method, it is surprising that it has not been noticed by earlier cereal workers. We noticed the difficulty and substituted gold electrodes for platinum in the summer of 1926, and a search of the literature has revealed the fact that the phenomenon has been observed by workers in other fields. It appears to be caused by the presence of oxidising and reducing salts.

Dixon and Quastel (1923), in a paper on certain reduction-oxidation systems such as cysteine-cystine, state that the R.S.H.-R.S.S.R. systems had hitherto been studied only from the point of view of reaction velocities. Electrometric evidence that such systems could be classed with the usual type of reversible oxidation processes was lacking, owing to the extraordinary difficulty of measuring the potentials when the ordinary platinum-calomel cell was used, owing to the occurrence of continuous and extensive drifts. They made enquiry into the nature of these drifts and stated that although it was as yet difficult to state their actual causes they had been successful in obtaining another cell, using gold instead of platinum, which proved to be practically free from them.

Corran and Lewis (1924), when measuring the pH of sheep's blood with the quinhydrone electrode using platinum, obtained highly improbable values such as pH 13, but by substituting a bright gold electrode for the platinum electrode they obtained satisfactory results. They state that "since platinum foil functions other than as an inert electrode (for example as a catalyst in the oxidation of quinol) gold foil was substituted."

Watson (1927) in a paper on the "use of quinhydrone electrode for following changes of pH in Swiss cheese" states "The electrodes first used were blades and wires of platinum. . . . After a few weeks the electrodes began to give very erratic results, showing a rapid drift and giving a pH reading of 3.86 instead of 3.97 with 0.5 m acid potassium phthalate. The electrodes were so badly poisoned that it was impossible to obtain correct values by any treatment until they were gold plated, after which they performed satisfactorily. . . . Pure gold electrodes were also used and found to be very satisfactory."

All the data given in Tables VII to XII and in Figures 1 to 3 were obtained by means of the quinhydrone electrode. *

Use of Filtered Extracts, Centrifuged Extracts, Suspensions and the Decantates from Suspensions that Have Settled in Measuring the H-Ion Concentration of Flours

In measuring the H-ion concentration of a flour, most workers have shaken the flour and water together, usually in the ratio of 1 part of the former to 10 parts of the latter, and having filtered or centrifuged the suspension have used the clear extract on which to make their measurements. We have found, however, that the H-ion concentration of the filtered extract is not always the same as that of the centrifuged extract, and that the H-ion concentration of both these is much lower than that of the suspension itself. If the suspension is allowed to settle and the clear supernatant liquid is used for measurement, its H-ion concentration is found to be the same as that of the centrifuged extract. This is shown in Table VII.

TABLE VII
COMPARISON OF H-ION CONCENTRATION DETERMINED BY QUINHYDRONE ELECTRODE:
OF DECANTATES AND CENTRIFUGED EXTRACTS

Decantate	Centrifuged extract	Difference
pH = 6.00	pH = 6.00	.00
6.02	6.04	+.02
6.06	6.06	.00
5.92	5.92	.00
6.13	6.13	.00
6.21	6.20	-.01
6.05	6.07	+.02
5.88	5.90	+.02
6.21	6.22	+.01
5.78	5.78	.00
6.12	6.11	-.01
6.34	6.37	+.03
6.07	6.06	-.01
6.07	6.06	-.01
6.27	6.27	.00

The difference between the H-ion concentration of the filtered extract and the decantate (obtained as described on p. 458) is shown in Table VIII, where it will be seen that the H-ion concentration of the filtered extract is usually equal to or lower than that of the decantate, the differences observed for the 34 pairs of determinations ranging from -0.02 to $+0.11$ of pH. It will be noticed that 12 of the 34 differences fall within the range of ± 3 times the probable error of the quinhydrone electrode and are not therefore significant. The remaining differences are well outside this range, the biggest being 11 times the probable error. Further, these 22 significant values are all of the same sign, which indicates that the differences are real and not due to accidental errors. The H-ion concentration of a flour-in-water suspension is higher than that of the filtered or centrifuged extract. This is shown by the following two experiments.

TABLE VIII
COMPARISON OF H-ION CONCENTRATION DETERMINED BY QUINHYDRONE ELECTRODE:
OF DECANTATES AND FILTERED EXTRACTS

Decantate	Filtered extract	Difference
pH = 5.83	pH = 5.90	+ .07
6.17	6.23	+ .06
6.29	6.31	+ .02
6.25	6.23	-.02
6.11	6.09	-.02
6.23	6.27	+ .04
6.15	6.18	+ .03
6.14	6.18	+ .04
6.30	6.34	+ .04
6.25	6.31	+ .06
6.50	6.49	-.01
6.51	6.50	-.01
6.20	6.27	+ .07
6.31	6.35	+ .04
6.30	6.38	+ .08
6.10	6.15	+ .05
6.22	6.27	+ .05
6.17	6.23	+ .06
6.42	6.41	+ .01
6.46	6.46	.00
6.15	6.14	+ .01
6.40	6.42	+ .02
6.47	6.49	+ .02
6.47	6.51	+ .04
6.52	6.62	+ .10
6.45	6.52	+ .07
6.35	6.44	+ .09
6.30	6.41	+ .11
6.58	6.60	+ .02
6.38	6.48	+ .10
6.37	6.43	+ .06
6.52	6.59	+ .07
6.48	6.55	+ .07
6.47	6.57	+ .10

A 10% flour suspension was poured into a tall vessel and at intervals the H-ion concentration of the bottom layers of the suspension was measured. As the flour concentration at the bottom of the vessel increased, the H-ion concentration also increased, as shown in Table IX.

TABLE IX
EFFECT OF TIME OF SETTLING ON H-ION CONCENTRATION OF SUSPENSION

Time of settling, min.	pH
0	5.88
7	5.84
14	5.79
22	5.75
30	5.72
39	5.70
48	5.69
60	5.685

In the second experiment, with a different flour, the suspension was allowed to settle and samples were taken at intervals from the top layers of solution and their H-ion concentrations were measured. As the top layers cleared by the settling of the flour particles, so the H-ion concentration decreased, i.e., pH increased, as is shown in Table X.

TABLE X
EFFECT OF TIME OF SETTLING ON H-ION CONCENTRATION OF A DECANTATE

Time of settling, min.	pH
0	6.06
5	6.11
10	6.13
15	6.145
20	6.165
25	6.18
30	6.185

These two experiments show that the presence of the flour particles increases the H-ion concentration. The reason for this is not altogether clear, but it may be connected with the existence of a Donnan equilibrium within the flour-water system. The problem is being further investigated.

Relationship Between H-Ion Concentration and Flour Concentration

Most workers in measuring the H-ion concentration of a flour have used 1 part of flour to 10 parts of water in making their extracts. This is the ratio generally used in the writers' laboratories in making routine measurements and was the ratio used in obtain-

ing the figures so far given in this paper. It has been found, however, that if the ratio of flour to water is varied, the H-ion concentration of the extract or suspension increases with increasing flour concentration. In Table XI the H-ion concentrations expressed in terms of pH are given for the centrifuged extracts obtained from a series of Hungarian flour 'divides.' The flour-water ratios employed varied from 1:10 to 1:2. The flours 0, 2, 4, 5, 6, and 7 represent increasingly low-grade flour milled from the same wheat mixture. (These six flour grades are among those normally sold in Hungary. They were made commercially on a nine-break milling system and would correspond to the following fractions of the wheat:

- 0 = part of the top 42 % of wheat,
- 2 = the fraction 42 to 52 % of the wheat, i.e., the top 10 %
after extraction of the 42 % of top patents,
- 4 = 50 to 60 %,
- 5 = 55 to 65 %,
- 6 = 58 to 72 %,
- 7 = 67 to 72 % of the wheat.

0 therefore corresponds to a short top patent flour and 7 to the bottom 5 % of an English flour stream.)

The figures in Table XI show that the difference in H-ion concentration between the weaker and the more concentrated extracts varies with the grade of flour, being greater the lower the flour grade. This point is also brought out in Figure 1 (the data of which are given in Table XI) where the change of H-ion concentration expressed as pH of the centrifuged extract is plotted against the flour concentration of the suspension used in making the extract. The curves for the Hungarian flours 2, 4, and 6 approach each other with increasing flour concentration. Beyond a flour-water ratio of 1:2 no liquid can be extracted in our centrifuge. (For our machine the value of the centrifugal force is about $2,000 \times g$). In Figure 1 curves are also given for the top 80% and the bottom 20% of a flour from an English mill. These two curves also approach each other with increasing flour concentration. The top 80% flour curve and the Hungarian 6 curve intersect; which brings out the interesting point that if a flour-water ratio of 1:2 were used, the extract from the Hungarian 6 flour would be found to have the greater H-ion concentration (smaller pH); while, on the other hand, if a ratio of 1:4 or more were used,

the extract from the top 80% flour would be found to have the greater H-ion concentration.

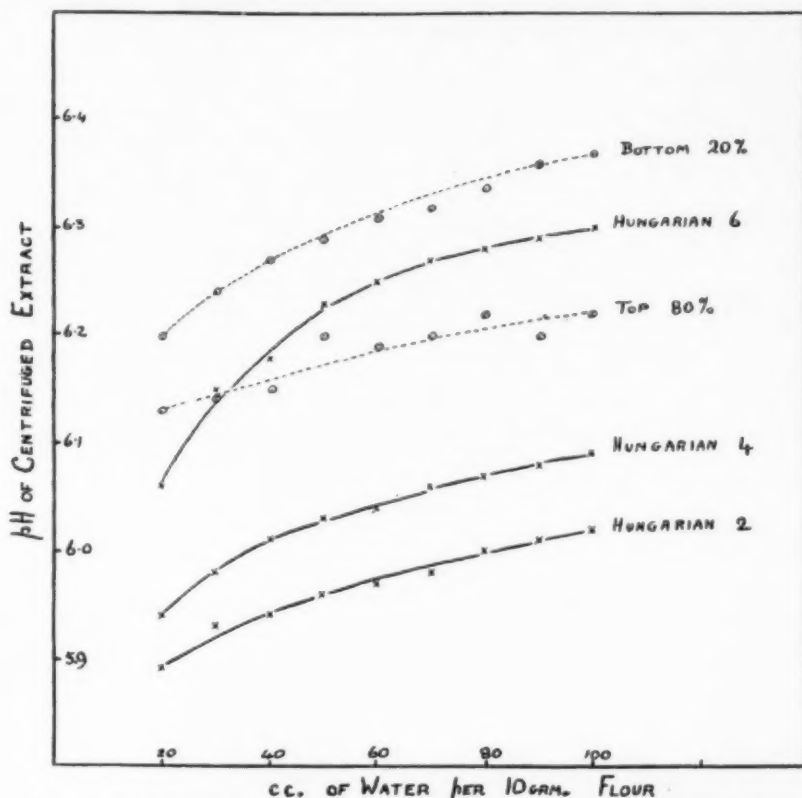


Fig. 1. Effect of Flour Concentration on H-Ion Concentration of Centrifuged Extracts

TABLE XI
EFFECT OF FLOUR CONCENTRATION ON H-ION CONCENTRATION
DETERMINED BY QUINHYDRONE ELECTRODE

Flour	Ratios Flour : Water									Diff. in pH between ratios 1:10 and 1:2
	1:10	1:9	1:8	1:7	1:6	1:5	1:4	1:3	1:2	
Hungarian 0	5.94	5.86	.08
Hungarian 2	6.02	6.01	6.00	5.98	5.97	5.96	5.94	5.93	5.90	.12
Hungarian 4	6.09	6.08	6.07	6.06	6.04	6.03	6.01	5.98	5.94	.15
Hungarian 5	6.21	6.00	.21
Hungarian 6	6.30	6.29	6.28	6.27	6.25	6.23	6.18	6.15	6.06	.24
Hungarian 7	6.29	6.04	.25
Mixed grist from English mill:										
Top 80%	6.22	6.20	6.22	6.20	6.19	6.20	6.15	6.14	6.13	.09
Bottom 20%	6.37	6.36	6.34	6.32	6.31	6.29	6.27	6.24	6.20	.17

In Figure 2 the curves are shown for the change in H-ion concentration of both the centrifuged extract and the suspension for

the same top 80% and bottom 20% flours. Like the curves for the extracts, the curves for the suspensions approach each other with increasing flour concentration. On the other hand, the curves for the extract and for the suspension of the same flour diverge with increasing flour concentration. This divergence is evidently connected with the factor (already referred to) present in a suspension which causes a suspension to show a greater H-ion concentration than that of the aqueous extract or decantate, a factor

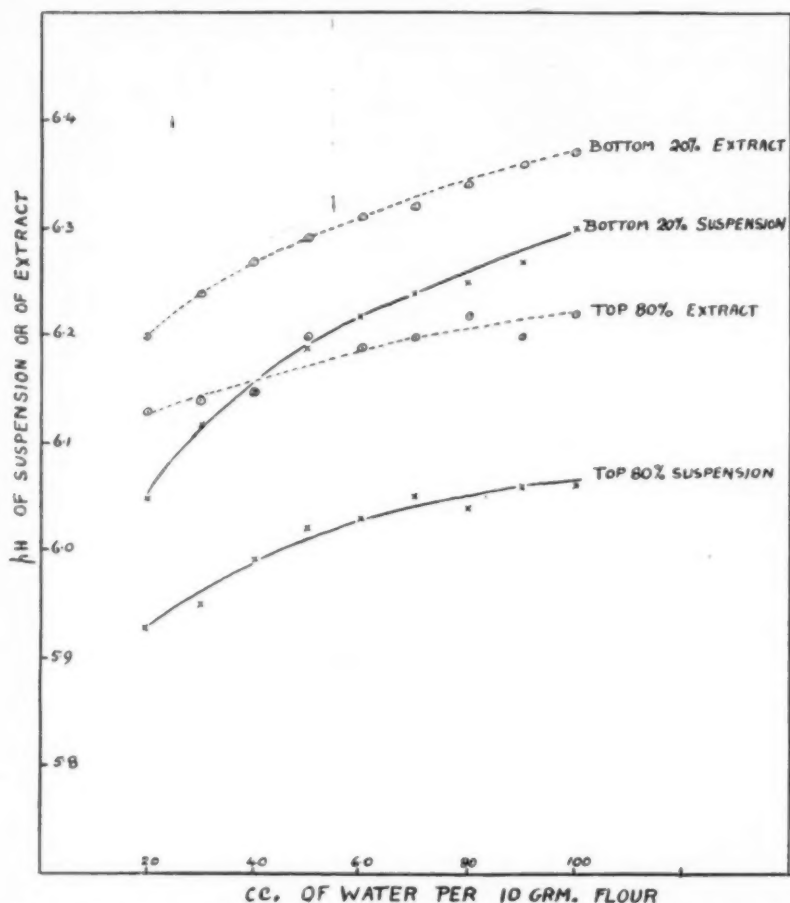


Fig. 2. Effect of Flour Concentration on H-Ion Concentration of Suspensions and of Centrifuged Extracts

that appears to increase in magnitude with increasing concentration. Attempts were made to trace the curves for the suspensions back to a flour-water ratio of 2:1, which corresponds to the ratio for a dough. The results, however, were not satisfactory, as the

quinhydrone electrode gave erratic and discordant results at such concentrations and the hydrogen electrode cannot be employed. Results point to the unexpected conclusion that a series of doughs made from a series of 'divides' (i.e., flours of different grades) from the same flour stream show strikingly small differences in H-ion concentration even if they do not turn out to be substantially the same. When determinations are made in the conventional manner, using flour-water ratios of 1 : 10, the H-ion concentrations of such divides may be, and usually are, widely different.

The problem of determining with reasonable accuracy the H-ion concentration of a dough is one of great theoretical interest and importance and is a necessary preliminary to extending our almost negligible knowledge of flour reaction. The experimental difficulties appear to be considerable and we are developing both the antimony and the glass electrodes in an attempt to solve the problem.

Effect of Time of Extraction on H-Ion Concentration

Bailey and Peterson (1921) shook flour-and-water mixtures for varying times up to 4 hours and measured the H-ion concentration of the centrifuged extracts at the end of each hour. They found that there was no appreciable change in H-ion concentration with time of extraction.

The writers have found that the H-ion concentration increases slightly with time of extraction, as is shown in Table XII.

TABLE XII
EFFECT OF TIME OF EXTRACTION ON H-ION CONCENTRATION

Time of extraction	H-ion concentration of centrifuged extract
hr.	pH = 6.02
$\frac{1}{2}$	6.00
1	5.97
2	5.91
$3\frac{1}{2}$	5.88
4 $\frac{1}{2}$	

The addition of auramine (1 part in 10,000 parts of solution) to delay bacterial action made no difference in the results. This change in H-ion concentration was found not to go on in the filtered or centrifuged extract. Once the flour had been separated, the H-ion concentration of the extract remained unchanged up to 3 hours, beyond which time measurements were not made.

Buffering Action of Flour

According to available literature, the buffering action of a flour is usually measured by adding a known quantity of acid to a filtered or centrifuged flour extract, and noting the change in H-ion concentration so produced. This method measures only the buffering action of the soluble constituents of the flour that have actually been dissolved out. The method the writers have adopted is to add the acid to the flour-water mixture, after which the H-ion concentration of the extract is determined in the usual way. The change in H-ion concentration produced in this way appears to us to be a better measure of the buffering action of the flour itself.

In Figure 3 the buffering action of the flour and of the extract are compared for 54 cases and, as can be seen, there appears to be no direct proportionality between the two values. The former may vary from $1\frac{1}{2}$ to $3\frac{1}{2}$ times the latter. There is, however, a general positive correlation between the two values, since the correlation coefficient r for the 54 cases given works out at 0.56 with a probable error of ± 0.06 . Bailey and Peterson (1921) found that the buffering action of a flour extract increased with time of extraction, the increase, they thought, being due to the phosphate produced from the phytin present in the flour by the action of the enzyme phytase during extraction. The buffering action of the flour, however, as measured by the writers, shows no change up to three hours' extraction, beyond which time measurements have not been carried out.

Routine Methods Used for Measuring the H-Ion Concentration and the Buffering Action of a Flour

Into each of two 200-cc. stoppered bottles a 10-gram sample of the flour is placed. To the first, 100 cc. of distilled water is added; and to the second, 90 cc. of distilled water and 10 cc. of N/100 lactic acid. After shaking at intervals for 30 minutes they are allowed to settle for not less than 15 minutes. (The time of settling depends on the width of the bottle and on the grade of flour, but the degree of settling can be judged from appearances. When a sharp, clear division is seen between the settled flour mass and the supernatant liquid and the latter appears uniform in turbidity [which should be slight] no change in H-ion concentration is noticeable on further standing. The 100 determinations mentioned on p. 449, of which the probable error was determined, were carried out in this way. The calculated probable error therefore includes any 'settling error.' That this error is small is further indicated by the close agreement between the results obtained for decantates and centri-

fuged extracts given in Table VII.) The H-ion concentrations of the supernatant liquids are then determined. That of the first is taken as the H-ion concentration of the flour and the difference between the two expressed as pH is taken as the buffer value of the flour.

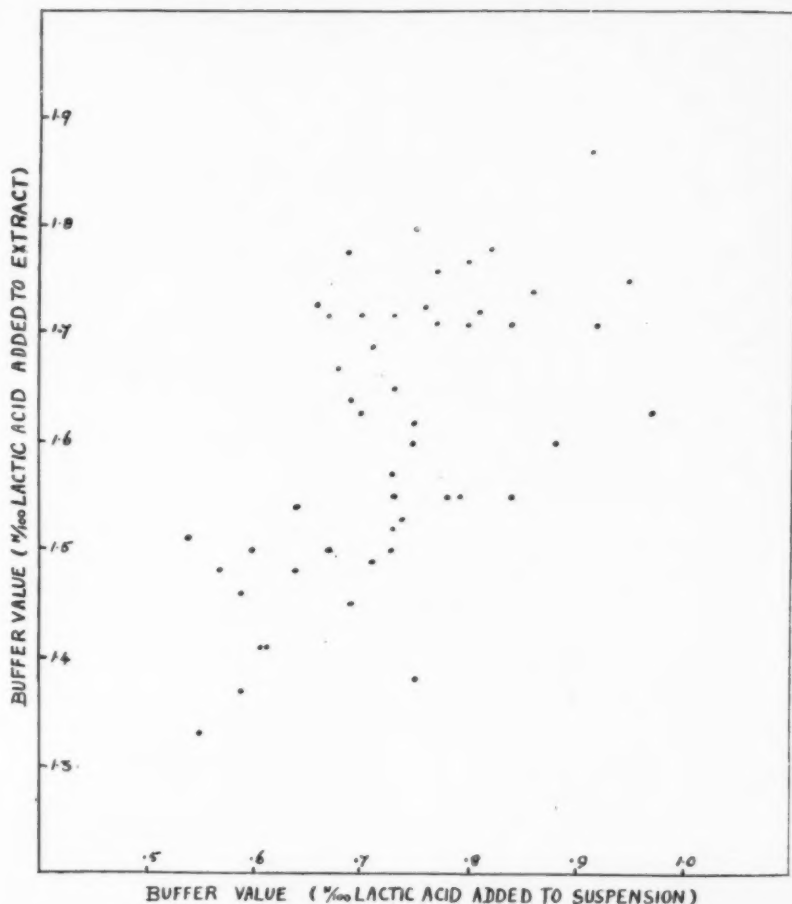


Fig. 3. Relation Between Buffer Effect of Flour and of Extracts

This method is substantially the same as the conventional method, but from what has been written above, the values so obtained must be regarded as purely conventional and arbitrary, or even empirical, values. The slopes of the curves in Figures 1 and 2 strongly suggest that such conventional values cannot be correlated with the H-ion concentrations of the doughs. And yet, it need hardly be pointed out in this connection, it is the H-ion concentration of the dough—rather than that of dilute flour-water mixtures—that is of real interest to cereal workers.

Summary

The electrometric method of determining H-ion concentration has been shown to be far more reliable than the colorimetric method.

The quinhydrone electrode gives results in satisfactory agreement with those obtained by means of the hydrogen electrode provided gold or gold-plated electrodes are employed. Quinhydrone with platinum electrodes gives unreliable results, errors in pH of the order of 0.4 or more not infrequently occurring.

Concordant values for H-ion concentration can be obtained with centrifuged extracts and with decantates from suspensions. Filtered extracts generally give slightly low values and suspensions always high values.

H-ion concentration of flour extracts increases as the ratio of flour to water increases. The slopes of the concentration-pH curves are different for different flours and curves for different flours may cross. Hence the H-ion concentration of flour extracts obtained in the conventional way cannot be correlated with the H-ion concentrations of the corresponding doughs.

The H-ion concentration of flour extracts appears to increase very slightly with increasing time of extraction.

The apparent buffer action of a flour is widely different from that of a flour extract, the former value varying from $1\frac{1}{2}$ to $3\frac{1}{2}$ times the latter.

Literature Cited

- Bailey, C. H. and Peterson, A. C.
1921 Studies of wheat flour grades. II. Buffer action of water extracts. *Ind. Eng. Chem.* **13**: 916.
- Biilmann, E.
1924 On the measurement of hydrogen-ion concentration in soil by means of the quinhydrone electrode. *J. Agr. Sci.* **14**: 232.
- Corran, J. W. and Lewis, W. C.
1924 The hydrogen-ion concentration of the whole blood of normal males and of cancer patients measured by means of the quinhydrone electrode. *Biochem. J.* **18**: 1358.
- Dixon, M. and Quastel, J. H.
1923 A new type of reduction-oxidation system. pt. I. Cysteine and glutathione. *J. Chem. Soc.* **123**: 2943.
- Watson, P. D.
1927 Use of quinhydrone electrode for following changes of pH in Swiss cheese. *Ind. Eng. Chem.* **19**: 1272.

EFFECT OF VARIATION IN THE METHOD OF MANUFACTURE ON THE BAKING QUALITY OF DRY SKIMMILK

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The work of Greenbank, Steinbarger, Deysher, and Holm (1927) in these laboratories has given evidence that the heat treatment of skimmilk prior to the manufacture of a dry milk greatly improves the baking quality of the product when incorporated in dough mixes. In their investigation, dry skimmilk that had been subjected to a relatively high heat treatment before being reduced to a powder gave better results when used in bread making than that subjected to a lower heat treatment.

This variation in baking quality as a result of forewarming seemed to warrant further study on the effects of the heat treatment of the milk.

Experimental

Preparation of Dry Skimmilk

Six samples of dry skimmilk were prepared for use in studying the effects of forewarming on baking quality. The milk used was produced by the dairy herd of the Bureau of Dairy Industry, at Beltsville, Maryland. Previous to drying, each sample of milk was held for 30 minutes at one of the following temperatures: 50°, 63°, 73°, 83°, 93°, and 100°C. It was impossible to make the samples on the same day because of the time consumed in cleaning the apparatus after each run. In order to use milk of approximately the same age the drying process was started each day at noon, using a mixture of milk of that morning and of the previous evening.

The milk was dried by the spray system. By means of a compression pump it was forced through the spray into the drying chamber at 1800-2500 pounds pressure. This drying chamber was heated for 30 minutes previous to use and maintained at about 160°C., tho the actual temperature of the dry product as it left the chamber was considerably lower.

The solubility of the powder, so far as can be determined, was not impaired.

Viscosity of the Reconstituted Milks

Previous work in these laboratories indicated that there is direct correlation between the body of the solution of a reconstituted dry skimmilk and its baking quality. To further test this observation the viscosities of the six dry milks to be used were determined.

The apparatus used to determine viscosity was a modification of the Ostwald type. Forty per cent solutions of the milks were prepared and held approximately 18 hours in the refrigerator to obtain equilibrium. After the initial viscosity reading, one gram of water was added. The solution was made uniform again by stirring carefully and the viscosity reading was taken a second time. This procedure was repeated until the difference between the reading before and after the addition of the water had no further significance. The temperature of the pipette was maintained at 25°C., by means of a water jacket. The results obtained by this procedure are recorded in Figure 1. There is a decrease in viscosity with forewarming temperatures from 50° to 73°C., a marked increase at 83°C., and again a slight decrease with the 93° and 100°C.

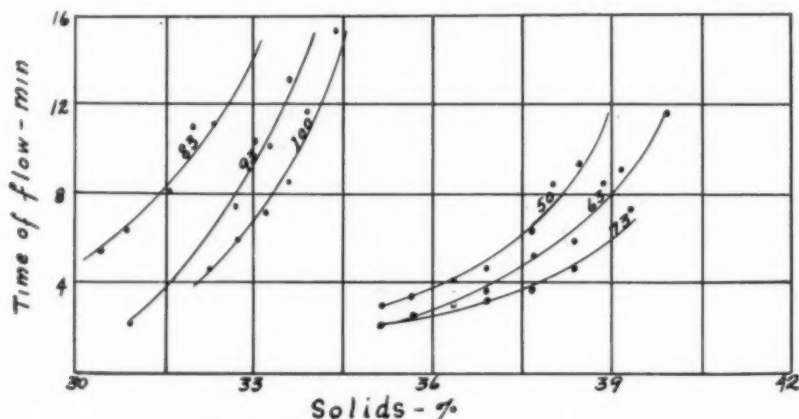


Fig. 1. Effect of Forewarming of Milk on Viscosity of Solution of Reconstituted Dry Product

As a rule, dry milks from milks heated to 83°C., when reconstituted, give solutions of lower body (viscosity) than those heated to higher temperatures. These results differ from all other results obtained to date in that reconstituted dry milk, prepared from the milk heated to 83°C., has a greater body than milks heated to higher temperatures. The reason for this exception in variation is not known.

Flours Used

A hard spring wheat flour, a hard winter wheat flour, and a soft winter wheat flour were used in the investigation. They were selected as representing the important wheat producing regions of the United States. The chemical analysis of the three flours is recorded in Table I.

TABLE I
COMPOSITION OF THE FLOURS (DRY BASIS)

Lab. No.	Kind of flour	Protein per cent	Ash per cent
1	Hard spring wheat	13.17	0.480
2	Hard winter wheat	11.52	.481
3	Soft winter wheat	9.45	0.458

Baking Results

The six samples of dry skimmilk described in the foregoing were used in bread making. The bread was made according to the formula described by Blish (1928) which has been accepted as the tentative standard experimental baking test by the American Association of Cereal Chemists. The following modifications of the basic formula and procedure were made:

1. Four per cent of dry skimmilk was used.
2. Absorption was modified according to that which gave the best results.
3. The fermentation cabinet was held at 27°C.
4. Fermentation time was one of the variants; periods ranging from 60 to 240 minutes were used at 15-minute intervals.
5. Flour sample No. 3—the soft winter wheat flour—was given a proof period of 50 minutes instead of 55 minutes.

The results on loaf volume obtained by this procedure with the three flours are recorded in Figures 2, 3, and 4.

The loaf volume of the bread made with dry skimmilk that had a forewarming temperature of 50°C. was smaller, with all three flours, than the loaf volumes of breads made with dry skim-milks that had higher forewarming temperatures. Likewise, the period of fermentation tolerance was shorter when dry skimmilk of 50°C. was used than when the milk had been held at a higher temperature.

The dry skimmilk with a forewarming treatment of 63°C. showed a slight improvement in the baking quality of bread, as to loaf volume and period of fermentation tolerance, over that with a 50°C. treatment.

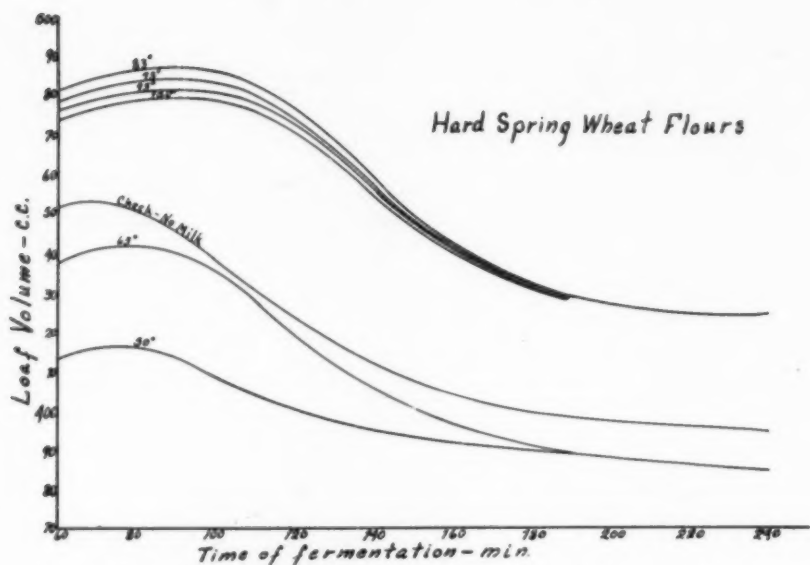


Fig. 2. Effect of Forewarming of Milk Used on Baking Quality of Hard Spring Wheat Flours

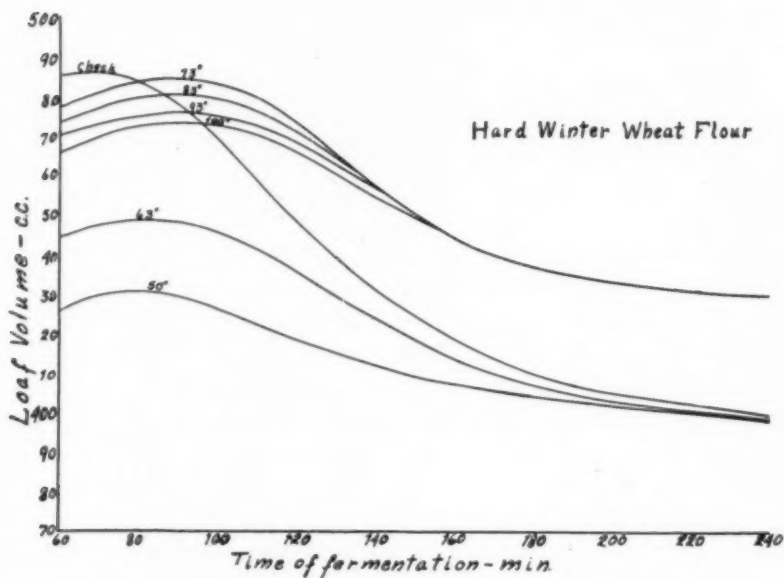


Fig. 3. Effect of Forewarming of Milk Used on Baking Quality of Hard Winter Wheat Flours

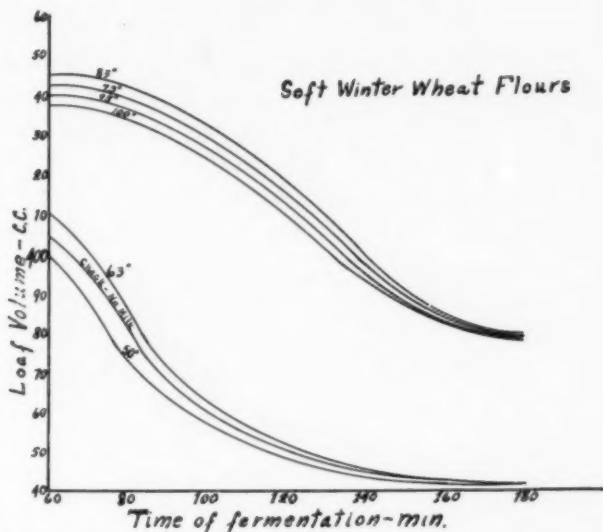


Fig. 4. Effect of Forewarming of Milk Used on Baking Quality of Soft Winter Wheat Flours

Only slight differences in loaf volume and fermentation tolerance were seen in breads made with milks that had been subjected to temperatures of 73°, 83°, 93°, and 100°C. previous to changing them to the dry state. This entire series showed much improvement in volume and fermentation tolerance over the breads of the 50° and 63°C. temperatures.

The loaf volume of the bread made from spring wheat flour in which no milk was used, was between that of bread that had received the forewarming treatment of 63°C. and those that had received the higher heat treatments. The bread made from the hard winter wheat flour that contained no milk was better in volume than that made from the doughs containing any of the six dry skim-milks with the shorter fermentation periods. With the hard winter wheat flour, as with the other flours, the period of fermentation tolerance was increased. The loaf volume of the bread made from the soft winter wheat flour, that contained no milk, was larger than the loaf made with milk that had the forewarming treatment of 50°C., but smaller than the one in which the milk had received a temperature of 63°C.

Improvements in size of break, grain, and texture, corresponding to the improvements in loaf volume, were obtained in the breads made with the milks that had been subjected to the higher heat treatments. Figures 5 and 6 are photographs of bread made

from Flour No. 1 on a 90-minute fermentation period. Grain and texture were better in the breads that contained no milk than in those made with milk that had been subjected to forewarming treatments of 50° and 63°C., but not so good as in the breads made with milks that had been subjected to higher temperatures. There was only slight variation in improvement in grain and texture of the bread when the milks used had been held at 73°, 83°, 93°, or 100°C. for 30 minutes.

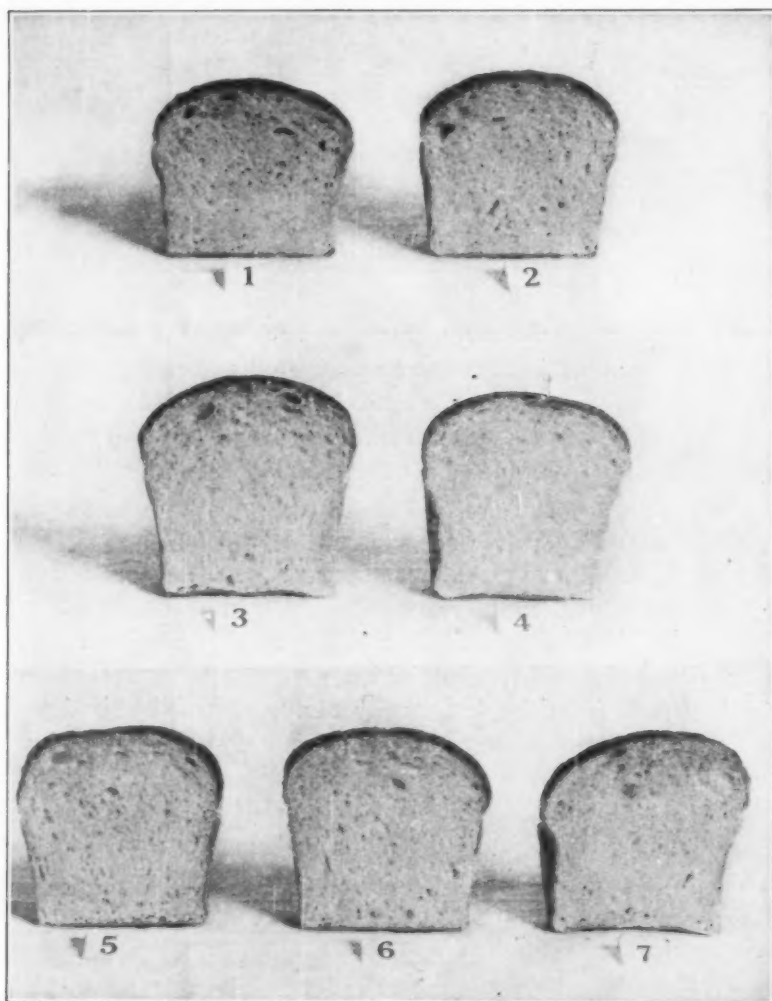


Fig. 5. Effect on Baking Quality of Forewarming Treatment of Dry Skimmilk Used

No. 7 contains no milk. Each of the other samples contains 4% dry skimmilk treated 30 minutes at the following temperatures: No. 1, 50°; No. 2, 63°; No. 3, 73°; No. 4, 83°; No. 5, 93°; No. 6, 100°C.

This greater improvement in all characteristics as a result of the higher forewarming treatments was found in all three flours. These findings confirm the work of Greenbank, Steinbarger, Deysher, and Holm (1927), with the exception that a direct correlation of baking quality and increased viscosity was not noted with the sample prepared from milk heated to 73°C.

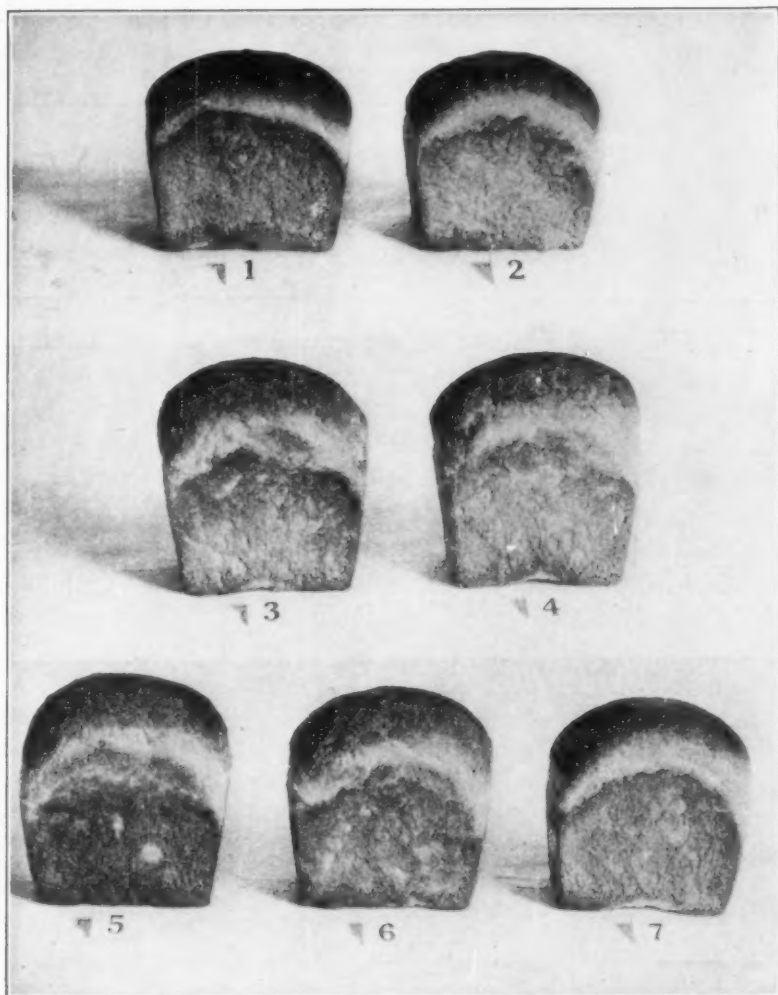


Fig. 6. Effect on Baking Quality of Forewarming Treatment of Dry Skimmilk Used
No. 7 contains no milk. Each of the other samples contains 4% dry skimmilk treated 30 minutes at the following temperatures: No. 1, 50°; No. 2, 63°; No. 3, 73°; No. 4, 83°; No. 5, 93°; No. 6, 100°C.

It is very necessary that water be used in sufficient quantities when dry skimmilk is incorporated in the dough mixtures. There is a variation in absorption with different milks. The results of absorption measurements obtained with these six samples are recorded in Table II.

TABLE II
EFFECT ON ABSORPTION OF DOUGHS WHEN DRY SKIMMILK IS INCORPORATED IN THE DOUGH
BATCH
(Flour sample No. 1)

Treatment of milk	Absorption
°C. min.	per cent
50-30	59.0
63-30	59.0
73-30	60.0
83-30	63.0
93-30	62.0
100-30	62.5
No milk used	58.0

There was an increase in absorption with increase in forewarming temperatures of the milks up to 83°C. Dough made with 4 per cent of the milk which had a forewarming temperature of 83°C. required 5 per cent higher absorption than dough from the same flour made without the use of milk.

The changes in milk, caused by heat, that are responsible for improved baking quality are not known. Studies on the effect of heat upon the variation in the soluble minerals normally found in milk, effect of heat treatment on albumin, and effect of heat treatment on buffer action, and their relations to bread quality are contemplated.

Summary

Six samples of dry skimmilk with forewarming treatments for 30 minutes at 50°, 63°, 73°, 83°, 93°, and 100°C. were prepared and used in this investigation.

One hard spring wheat flour, one hard winter wheat flour, and a soft winter wheat flour were used in studying the baking qualities of the six samples of dry skimmilk.

The three kinds of flour differed in their reaction to dry skimmilk. The greatest improvement in baking as the result of the use of dry skimmilk was with the soft winter wheat flour. The least improvement was noted with the flour made from hard winter wheat.

The range of fermentation time in which doughs give good bread is increased by the use of dry skimmilk. This is a very important factor as it adds to the ease with which doughs are handled in the bakery.

Loaf volume, period of fermentation tolerance, grain, texture, and break were used in scoring the bread. In the three flours the poorest results in all properties were obtained in the bread containing dry skimmilk that had been subjected to a temperature of 50°C. for 30 minutes previous to changing to the dry state. The forewarming temperature of 63°C. gave a slightly better result than that of 50°C. There was marked improvement in the baking quality when the milks had been given one of the four higher temperatures—73°, 83°, 93°, and 100°C., but the variation within the latter series was only slight.

Acknowledgments

The authors are indebted to P. A. Wright for the viscosity determinations and to S. A. Hall, of the Dairy Research Laboratories, for the preparation of the dry skimmilk samples.

Literature Cited

- Blish, M. J.
1928 Standard experimental baking test. Report of the committee of the American Association of Cereal Chemists. *Cereal Chem.* 5: 158-161.
- Greenbank, Geo. R., Steinbarger, Mable C., Deysher, E. F., and Holm Geo. E.
1927 The effect of heat treatment of skim milk upon the baking quality of the evaporated and dried products. *J. Dairy Sci.* 10: 335-342.
- Humphries A. E.
1905 The improvement of English wheats. National Assn. British and Irish Millers. Liverpool.

VOLUME DISPLACEMENT OF SALT-SUGAR SOLUTIONS

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The formula which has been accepted in the tentative standard baking test by the American Association of Cereal Chemists and described by Blish (1928) is as follows:

Flour—100 grams on a 15 per cent moisture basis

Yeast—3 grams

Salt—1 gram, 99.5 per cent pure

Sugar (Sucrose)—2.5 grams

Water (Distilled)—To 58 per cent absorption with flour on a 15 per cent moisture basis.

A salt-and-sugar solution offers a satisfactory means of adding these two ingredients to the dough batch. Quantities of 25, 50, or 100 cubic centimeters of the solution can be used at one time, depending upon the concentration and the number of loaves to be mixed. When the solution is added to the dough mixture the amount of water present per unit volume of solution must be known because it is a factor in absorption.

When yeast is used as a suspension, its volume displacement must be known. Shollenberger, Marshall, and Coleman (1924) found that 10 grams of yeast occupy 8.5 cubic centimeters when suspended in 38.5 cc. of water. From these figures it seems that 3 grams of yeast, the amount used in the above formula, would occupy 2.5 cc.

This paper presents data on the quantity of water to be added when salt-and-sugar solutions sufficient for several loaves are prepared at a time, and also the quantity of water to be allowed on absorption when these solutions are used in the dough mixture.

Experimental

Solutions in quantities of 500 cc. were prepared by putting 10 grams of salt and 25 grams of sugar in a volumetric flask. They were made up to the required volume with distilled water at 20°C. These solutions gave concentrations such that 50 cc. of each contained 1 gram of salt and 2.5 grams of sugar, the necessary amount of these two ingredients for one loaf. In like manner solutions containing 2, 2.5, 3, 4, 5, and 6 times this concentration were pre-

pared. Density determinations were made on solutions of these various concentrations. The densities obtained from this procedure are recorded in the third column of Table I. The volume occupied by the water, which is a factor in the absorption by the doughs, is recorded in the fourth column of Table I.

TABLE I

DENSITIES OF SOLUTIONS AND VOLUMES OCCUPIED BY WATER AND BY SALT AND SUGAR IN 50 CC. OF SOLUTIONS OF VARIOUS CONCENTRATIONS

Salt	Sugar	Density of solutions	Volume occupied by the water	Volume occupied by the salt and sugar
gm.	gm.		cc.	cc.
1.0	2.5	1.0332	48.16	1.84
2.0	5.0	1.0655	46.27	3.72
2.5	6.25	1.0821	45.35	4.65
3.0	7.5	1.0980	44.40	5.60
4.0	10.0	1.1304	42.52	7.47
5.0	12.5	1.1615	40.57	9.43
6.0	15.0	1.1923	38.61	11.39

Data regarding solutions of different concentrations for one or more doughs are recorded in Table II, which is prepared by taking multiples of the data in the fourth column of Table I.

TABLE II

CUBIC CENTIMETERS OF WATER REQUIRED IN SALT-AND-SUGAR SOLUTIONS OF DIFFERENT CONCENTRATIONS FOR ONE OR MORE DOUGHS

No. of doughs	Salt, gr.	1.0	2.0	2.5	3.0	4.0	5.0	6.0
	Sugar, gr.	2.5	5.0	6.25	7.5	10.0	12.5	15.0
		cc.	cc.	cc.	cc.	cc.	cc.	cc.
1		48	46	45	44	43	41	39
2		96	92	91	89	85	81	77
3		144	139	136	133	128	121	116
4		193	185	181	178	170	162	154
5		241	231	227	222	213	202	193
6		289	278	272	266	255	242	232
7		337	324	317	311	298	283	270
8		385	370	363	355	340	323	309
9		433	416	408	400	383	363	347
10		482	463	453	444	425	404	386
11		530	509	499	488	468	444	425
12		578	555	544	533	510	484	463
13		626	602	589	577	553	525	502
14		674	648	635	622	595	565	540
15		722	694	680	666	638	606	579
16		771	740	726	710	680	646	618
17		819	787	771	755	723	686	656
18		867	833	816	799	765	727	695
19		915	879	862	844	808	767	734
20		963	925	907	888	850	807	772

To illustrate the use of this table, let us assume that it is desired to have a sugar-and-salt solution for 18 loaves of bread, in each of which 100 grams of flour is used. Forty-five grams of sugar and 18

grams of salt together with 867 cc. of water are placed in a flask. The sugar and salt are dissolved. This will give a 900-cc. solution, or 18 portions of 50 cc. each; and in each 50 cc. there will be 2.5 grams of sugar and 1 gram of salt. In each 50 cc. of solution there are 48.2 cc. of water, which is a factor in calculating absorption. If three loaves instead of one are made from each of 18 flours, then 135 grams of sugar and 54 grams of salt are added to 799 cc. of water and 44.4 cc. is the amount of water in the 50 cc. of solution, which must be considered in calculating absorption. When 400, 500, or 600 grams of flour are made into dough it is advisable to use 100 cc. of the sugar-salt solution. For this purpose figures in the second, third, and fourth columns may be used. When one loaf of bread is mixed at a time, 25 cc. of solution may be added by using the amounts given by figures in the second column.

Summary

A solution of salt and sugar offers a convenient means of adding these two ingredients to the dough mixture.

The quantity of water used in this solution must be known because of its presence as a factor in absorption. A table is given for the concentration ordinarily used in bread making according to the formula reported by Blish (1928). A table is also given for volume displacement of salt and sugar when solutions for one or more doughs are prepared at the same time.

Literature. Cited

Blish, M. J.

1928 Standard experimental baking test. Report of committee of the American Association of Cereal Chemists. *Cereal Chem.* 5: 158-161.
Shollenberger, J. H., Marshall, W. K., and Coleman, D. A.

1924 Experimental milling and baking. U. S. Dept. Agr. Bull. 1187.

THE DICARBOXYLIC AMINO ACID FRACTION IN GLIADIN¹

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Because of the extensive use of wheat for human food, more attention has probably been given to the proteins of this cereal than to any other vegetable protein. Wheat gliadin, the alcohol-soluble protein, comprises approximately half the protein content of white wheat flour. Gliadin is unique in that, on hydrolysis, it yields more than half its weight of dicarboxylic amino acids (aspartic, glutamic, and hydroxyglutamic acids), a larger proportion of acids of this class than has been found in any other protein. Osborne and Guest (1911) isolated from gliadin 43.7 per cent of glutamic acid, and Dakin (1919) obtained 2.4 per cent of hydroxyglutamic acid. Recently Jones and Moeller (1928) found 0.8 per cent of aspartic acid. Together, these figures amount to 46.9 per cent of the gliadin. By making use of Foreman's method for the separation of glutamic and aspartic acids by precipitation of their calcium salts with alcohol, the total dicarboxylic amino acid fraction can be almost quantitatively separated from protein hydrolysates. Working recently with gliadin in another connection, we observed that the total dicarboxylic amino acid fraction separated by Foreman's (1914) method amounted to considerably more than the 46.9 per cent previously isolated as glutamic, aspartic, and hydroxyglutamic acids. This indicated that either one or more of these amino acids are present in gliadin in quantities larger than those heretofore reported, or that gliadin contains some other dibasic amino acid.

Because of the interest and importance attached to gliadin, we made a special study in order to isolate and account for as much as possible of the dicarboxylic amino acid fraction that gliadin yields on hydrolysis. Two separate lots of gliadin were hydrolyzed, one for 20 hours and the other for 46 hours. The quantity of the dicarboxylic amino acid fractions obtained in both cases was almost identical, amounting to 53.6 per cent of the gliadin. Of this quantity, 51.2 per cent was isolated as pure aspartic, glutamic, and hydroxyglutamic acids, leaving 2.4 per cent of the whole fraction unaccounted for. We believe that most, if not

¹ A preliminary report of this work was presented at the Seventy-Fifth Meeting of the American Chemical Society held in St. Louis, April 16 to 19, 1928.

all, of this difference was due to incomplete recovery of glutamic and hydroxyglutamic acids. As only pure products were weighed, there would inevitably be some loss. The percentages of glutamic acid found in the two lots, altho not in as close agreement as might be desired, are not far apart. The highest figure, 43 per cent, agrees fairly well with that found by Osborne and Guest. Both lots yielded the same quantity of aspartic acid (0.5 per cent). A large number of determinations of aspartic acid in gliadin have been made both in this laboratory and by other investigators, nearly all of which have yielded results within the range of 0.5 to 0.8 per cent.

The greatest difference between the percentages of the amino acids that we have found and those previously reported lies in the percentage of hydroxyglutamic acid. The quantity of this amino acid actually present in gliadin is doubtless higher than the 7.7 per cent we isolated.

Apparently the difference in the time of hydrolysis of the two lots of gliadin had no appreciable effect on the quantities of dicarboxylic amino acids formed. The total fractions obtained in both cases were the same. The small variations in the percentages of the individual amino acids isolated from the two lots of gliadin are doubtless to be ascribed to losses involved in their separation rather than to the difference in the time of hydrolysis.

Experimental

Some of the gliadin used in this work was obtained according to the method of Blish and Sandstedt (1926) from gluten prepared from a well known brand of hard wheat flour. The bulk of the protein, however, was prepared by a modified method. Moist gluten was twice extracted with 70 per cent alcohol. The joint alcoholic extracts were filtered through paper pulp, and most of the alcohol in the filtrates was removed at room temperature by blowing a current of air over the extracts contained in shallow trays. The gliadin settled out as a thick, viscous sirup. The supernatant liquid, consisting mostly of water, was decanted off, and the crude gliadin dissolved in 0.07 N acetic acid. The gliadin was reprecipitated by addition of lithium chloride to the acetic acid solution. The precipitate was then redissolved by adding enough 95 per cent alcohol to the moist material to bring the concentration of alcohol in the mixture to approximately 70 per cent. The solution was filtered and slowly poured into several volumes of absolute alcohol. The precipitated gliadin was then dried in the usual way by successive treatments with absolute alcohol and ether. It contained 17.81 per cent nitrogen, calculated on an ash- and moisture-free basis.

The gliadin was hydrolyzed in two separate lots of 226.7 gm. each (ash-and moisture-free) by boiling with 1000 cc. of 20 per cent hydrochloric acid. Lot I was hydrolyzed for 20 hours and Lot II for 46 hours.

After hydrolysis both lots were handled in the same way throughout the subsequent analyses.

The hydrolysates were diluted and filtered. After being concentrated at reduced pressure at a temperature not exceeding 50° C., the solutions were saturated with hydrochloric acid gas, and most of the glutamic acid was removed as the hydrochloride in the usual way.

The amino acids remaining in the filtrates from the glutamic acid hydrochloride were converted into their barium salts, and the dicarboxylic amino acid salts separated by precipitation with alcohol.² The precipitated barium salts of this fraction were redissolved in water and again precipitated with alcohol. After quantitative removal of barium the free dicarboxylic amino acids were obtained and thoroly dried. This fraction contains almost quantitatively the dicarboxylic amino acids in the protein hydrolyzed with the exception of the glutamic acid removed directly from the hydrolysate as the hydrochloride. It usually also contains some pyrrolidone carboxylic acids, formed as secondary products by loss of a molecule of water from glutamic and hydroxyglutamic acids. Traces of other amino acids are generally present, notably tyrosine.

This mixture was exhaustively extracted at room temperature with glacial acetic acid, which dissolves the hydroxyglutamic and pyrrolidone carboxylic acids. The aspartic and glutamic acids that remained undissolved in the mixture were isolated and determined in the usual way. The aspartic acid was weighed in the form of pure copper aspartate, and the glutamic acid as the hydrochloride.

As much as possible of the acetic acid was removed from the acetic acid extracts by distillation under reduced pressure at 40° to 45° C. The sirupy residue was treated with absolute alcohol in order to remove any pyrrolidone carboxylic acids that may have been present. These compounds are soluble in alcohol. Very little material was dissolved by the alcohol, and the sirupy residue changed to a friable product that could be easily reduced to a powder. It was redissolved in water and reprecipitated with absolute alcohol. This process was again repeated, and the precipitate dried for three days *in vacuo* over phosphorus

² The details of the method for the precipitation of the barium salts of this fraction of amino acids, and for the separation of the individual amino acids have been fully described in several previous publications (Jones and Moeller [1928], Foreman [1924], and Kingston and Schryver [1924], so it is unnecessary to repeat them here.

pentoxide. Small quantities of impurities in the hydroxyglutamic acid were removed by means of phosphotungstic acid.

The hydroxyglutamic acid was further purified by converting it into the silver salt. The free acid was finally dried *in vacuo* over phosphorus pentoxide at room temperature. Analyses showed the hydroxyglutamic acid to have the following percentage composition: C, 36.69; H, 5.85 (theoretical C, 36.81; H, 5.52). In 20 per cent hydrochloric acid it showed a specific rotation of $+17^\circ$ C. This is in close agreement with the mean of several determinations made by Dakin (1919) on this amino acid ($+16.3^\circ$). The silver salt contained 57.12 per cent silver (theoretical 57.26 per cent).

The results of these analyses of gliadin are summarized in Table I.

TABLE I
SUMMARY OF THE DETERMINATIONS OF DICARBOXYLIC AMINO ACIDS IN GLIADIN*

Gliadin	Glutamic acid			Aspartic acid
	Isolated directly from the hydrolysate as the hydrochloride	Isolated from the barium salts	Total isolated	Total isolated
	per cent	per cent	per cent	per cent
Lot I	33.8	7.4	41.2	0.5
Lot II	34.2	8.7	43.0	0.5

	Hydroxyglutamic acid	Amino acids	Dicarboxylic amino acids	Dicarboxylic amino acid fraction
	Total isolated	Total recovered from barium salts	Total isolated and identified	Total precipitated as barium salts
	per cent	per cent	per cent	per cent
Lot I	7.3	19.8	49.0	53.6
Lot II	7.7	19.4	51.2	53.6

* The percentages are calculated on the basis of the ash- and moisture-free gliadin.

† Lot I was hydrolyzed for 20 hours, and Lot II for 46 hours.

Summary

Gliadin is unique in that it yields on hydrolysis over half its weight of dicarboxylic amino acids (aspartic, glutamic, and hydroxyglutamic acids), a proportion of this class of amino acids larger than has been found in any other protein. When hydrolyzed by boiling with 20 per cent hydrochloric acid, gliadin yielded 53.6 per cent of amino acids representing the dicarboxylic amino acid fraction as obtained by precipitation of their barium salts with alcohol. Of this quantity there were isolated the following percentages of pure amino acids: Glutamic acid, 43.0; hydroxyglutamic acid, 7.7; aspartic acid, 0.5. Length of time of hydrolysis of the gliadin (20 and 46 hours) had no significant effect on the proportions yielded of these amino acids.

Literature Cited

- Blish, M. J., and Sandstedt, R. M.
1926 An improved method for the preparation of wheat gliadin. *Cereal Chem.* 3: 144-149.
- Dakin, H. D.
1919 On amino-acids. Part II. Hydroxyglutamic acid. *Biochem. J.* 13: 398-429.
- Foreman, F. W.
1914 Quantitative estimation of aspartic and glutaminic acids in the products of protein hydrolysis. *Biochem. J.* 8: 463-480.
- Jones, D. B., and Moeller, O.
1928 Some recent determinations of aspartic and glutamic acids in various proteins. *J. Biol. Chem.* 79: 429-441.
- Kingston, H. L., and Schryver, S. B.
1924 Investigations of gelatin. Part III. The separation of the products of hydrolysis of gelatin by the carbamate method. *Biochem. J.* 18: 1070-1078.
- Osborne, T. B., and Guest, H. H.
1911 Analysis of the products of hydrolysis of wheat gliadin. *J. Biol. Chem.* 9: 425-438.

STALING AND HYDROGEN-ION CONCENTRATION

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There are persons who assert that among the different processes that take place during the staling of bread, the change of the acidity plays a special part; some state that it increases, others that it decreases, and, though the first statement is hardly supported by experimental facts, such opinions are expressed, especially in the larger books dealing with food-chemistry.

Before coming to the essence of the question, mention should be made of the substances to which acid reaction of bread can be traced.

Acid reaction, according to K. B. Lehmann (1893) is caused by at least two different factors: (1) free organic acid, (2) acid potassium phosphate, which comes into existence by the interaction of the organic acid resulting from the fermentation of the dough and the neutral phosphates preëxistent in the flour.

Lehmann detected in the part that is ether-soluble the following: (1) volatile acids, of which the chief part is acetic acid; traces of formic acid (eventually aldehyde). Butyric acid could not be detected. (2) A non-volatile acid, soluble in ether and water, which has proved to be lactic acid. (3) A higher sort of fatty acid, appearing in various quantities, which is non-volatile, is insoluble in water, stands probably near

to oleic acid, and is perhaps the decomposition product of the fat of the flour.

The part that is insoluble in ether can be largely dissolved in water. As this part contains so much phosphoric acid that its acidity, with the supposition of this being caused by potassium monophosphate, can be entirely explained and, moreover, since the water extract shows a different reaction with litmus and phenolphthalein, it can be accepted as finally proved that the acid phosphates also play a rôle in the acidity of bread.

The weak acidity of the part remaining after the extraction by ether and water is probably caused by proteins.

Nessler (1893) found the following acid content, expressed as lactic acid in per cent.

	Biscuit	Small loaf of finest wheat bread	Bread made with milk	Brown bread
	%	%	%	%
Acid content July 29	0.09	0.10	0.11	0.14
" " " 30	0.31	0.11	0.13	0.14
" " August 1	0.52	0.13	0.17	0.14
" " " 3	0.52	0.23	0.27	0.25

Lehmann in his first publication (1893) dealing with the acidity of bread during keeping, questioned the correctness of Nessler's facts, and later (1902) in a detailed consideration of the question was able to prove them false. He has shown that the acidity of bread kept in a **covered glass vessel remains the same**. On the other hand, uncovered bread loses a portion of the acid slowly at room temperature and more rapidly at higher temperature.

ACIDITY IN TERMS OF NORMAL ALKALI REQUIRED TO NEUTRALIZE 100 GRAMS OF CRUMB,
PHENOLPHTHALEIN AS INDICATOR

	Time of storage	Fresh bread	After storage
		Covered, kept cool	
"Graubrot"	5 days	8.8-9.0	9.2
" "	4 weeks	18.5	18.6
"Sauerbrot"	5 days	21.3-21.7	21.6
		Uncovered, kept at 40-50° C.	
"Graubrot"	5 "	21.3-21.7	20.4
		Uncovered, dried at 100° C. during 4 hours	
" "	4 hours	17.8	17.2-17.6
" "	"	16.0	15.2
" "	"	8.0	7.6

Barnard and Bishop (1914) investigated the effect of wrapping fresh bread with semi-porous waxed and paraffined paper upon the outer

peculiarities and the chemical composition during a period of 6 days. They used straight dough pan bread, straight dough rye bread, straight dough Vienna hearth bread, and sponge dough Bohemian rye bread, and their observations included the determination of acidity by titration.

The work of these authors shows conclusively that lactic acid acidity does not develop either in wrapped or unwrapped loaves of ordinary bread. A reference to their chart clearly shows that the acid content remains almost constant, varying little throughout the period during which the loaves were under observation.

They mention also the investigations of White (1910). His results are summarized as follows: Bread made under clean conditions from a good quality of flour and yeast does not grow acid, whether wrapped or not, even after 108 hours. (Bread wrapped while warm and bread wrapped while hot showed an increase in acidity in the inside portion of the loaf as compared with the crust. This increase amounts to 9% in the hot wrapped bread.)

Heiduschka and Deininger (1920) obtained similar results. In their work the following facts are to be found:

ACIDITY OF BREAD WHEN FRESH AND AFTER STORAGE, IN TERMS OF NORMAL ALKALI REQUIRED TO NEUTRALIZE THE AQUEOUS EXTRACT OF 100 GRAMS OF CRUMB

Experiment 3		Experiment 4		Experiment 5	
Fresh	11.43	Fresh	21.30	Fresh	16.90
After 14 days	10.59	After 17 days	20.80	After 14 days	16.83

All the investigators mentioned measured the "titratable acidity." The author did not get results by titration, but by measuring the hydrogen-ion concentration in the electrometric way, which method, with due precaution, is more sensitive and punctual. Publications on investigations of this kind, dealing with the staling of bread, have not been made, so far as the author is aware.

After some colorimetric experiments 0.2 molar KH-phtalate + 0.2 molar NaOH: indicator methyl red (pH = 4.0 — 6.4) (note Kent-Jones, 1924, pp. 276-282) and Michaelis's p-nitro-phenol series (pH = 5.4 — 7.0), which was employed for further orientation, the principal experiments were conducted in the electrometric way, as mentioned above.

Omitting a detailed description of the apparatus,¹ a Leeds & Northrup potentiometer, calibrated for saturated calomel electrode; a galvanometer for the null point instrument, and a storage cell of large ca-

¹ More detailed parts of the measuring method and experimental disposition can be found in the book of Kent-Jones pp. 282-91. General orientation, regarding everything, is given in the book of W. M. Clark: The determination of hydrogen-ions. Baltimore. 3rd ed. 1925.

capacity for source of current were used in these measurements. The saturated calomel electrode and the Bailey hydrogen electrode were used.

The hydrogen was generated with sulphuric acid in a Kipp apparatus, from the purest granulated zinc.

Two equal loaves for these experiments were made from the different flours with water, salt, and yeast. After cooling, these were weighed, one was put aside untouched, and twice 10 grams of average material was taken from the crumb of the other. This was broken into tiny pieces, shaken energetically in a 250-ccm. Erlenmeyer flask with 100 ccm. CO₂-free distilled water in a shaking apparatus moving horizontally and allowed to settle for 15 minutes. The decanted liquid was centrifuged in air-tight stoppered centrifugal tubes with 3500 r.p.m. for 15 minutes.

The other loaf of bread, after being stored for 48 hours, was prepared for the acidity determination in the same manner, taking into consideration the loss of weight.

The centrifuged extract was not filtered because, taking no account of the process of the CO₂-free filtering being very much complicated, it is not necessary, as K. B. Lehmann and Th. Paul state it.

The centrifuged extract was placed in the Bailey electrode, some purified hydrogen was introduced, the electrode was stoppered with a ground-in stopper, shaken during 3 minutes, and after coming into equilibrium the H-ion concentration was determined.

Table I shows the results from the experiments with wheat breads, Table II shows the same with rye breads.

TABLE I
HYDROGEN-ION CONCENTRATION OF FRESH AND STALE WHEAT BREADS

Expt.	*Flour No.	Fresh		After 48 hours	
		pH	[H]	pH	[H]
1	Os	5.81	0.16×10^{-5}	5.83	0.14×10^{-5}
2	Os	5.91	0.13×10^{-5}	5.92	0.12×10^{-5}
3	Og	5.87	0.14×10^{-5}	5.94	0.12×10^{-5}
4	Og	5.89	0.13×10^{-5}	5.95	0.11×10^{-5}
5	4	6.06	0.87×10^{-6}	6.14	0.73×10^{-6}
6	4	6.04	0.91×10^{-6}	6.09	0.82×10^{-6}
7	4	6.04	0.91×10^{-6}	6.13	0.75×10^{-6}
8	4	6.09	0.82×10^{-6}	6.14	0.73×10^{-6}

* Hungarian classification. / Os and Og fine white, 4 medium wheat flours; \bar{O} finest rye flour; O/I, fine rye flour/.

TABLE II
HYDROGEN-ION CONCENTRATION OF FRESH AND STALE RYE BREADS

Expt.	*Flour No.	Fresh		After 48 hours	
		pH	[H]	pH	[H]
9	\overline{O}	6.20	0.63×10^{-8}	6.28	0.53×10^{-8}
10	\overline{O}	6.23	0.59×10^{-8}	6.29	0.51×10^{-8}
11	O/I	6.30	0.50×10^{-8}	6.36	0.44×10^{-8}
12	O/I	6.28	0.53×10^{-8}	6.35	0.45×10^{-8}

* See footnote to Table I.

From the tables it can be seen that, contrary to the general point of view (mentioned above), results justify the investigators who state that *the acidity does not increase during ordinary keeping at room temperature, but either remains constant or shows some decrease.*

It must not be forgotten, however, that the acidity of perfectly stale bread can increase during further keeping, but this can be traced back to the activity of microorganisms as indicated by Barnard and Bishop (1914). It is possible that the peculiar facts of Nessler can thus be partially explained.

Literature Cited

- Barnard, H. E., and Bishop, H. E.
 1914 The effect of bread wrapping on the chemical composition of the loaf. *J. Ind. Eng. Chem.* **6**: 736-746.
- Heiduschka, A., and Deininger, J.
 1920 Beiträge zur Chemie der hochausgemahlenen Mehle und der daraus hergestellten Brote. *Z. unter. Nahr. Genussmtln.* **40**: 161-191.
- Kent-Jones, D. W.
 1924 *Modern Cereal Chemistry.* Liverpool.
- Lehmann, K. B.
 1893 Hygienische Untersuchungen über Mehl und Brot. III. Qualitative und quantitative Untersuchungen über den Säuregehalt des Brotes. *Archiv. Hyg.* **19**: 363-409.
- 1902 X. Neue Studien über die Acidität des Brotes, ihre Ursachen und ihre beste Bestimmungsmethode. *Archiv. Hyg.* **44**: 214-237.
- Nessler, J.
 1893 Cited by König: *Chemie der menschlichen Nahrungs und Genussmittel*, 3d ed., II. 615.
- White, H. L.
 1910 Acidity of wrapped bread. *No. Dak. Agr. Expt. Sta. Spec. Food Bull.*, **1**, p. 214.

NOTE ON THE GASOMETRIC DETERMINATION OF CARBON DIOXIDE BY THE CHITTICK METHOD

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Attention is called to the omission in the Chittick method (A.O.A.C. Book of Methods, 1925, p. 305) for the gasometric determination of carbon dioxide in baking powder, self-rising flour, etc., of a factor to correct the carbon dioxide gas volume reading for the partial displacement due to the vapor tension of the reagent, dilute sulfuric acid, used. This omission under certain circumstances may cause an appreciable error.

In the execution of this method it is observed that the addition of a measured volume of reagent-acid to the *dry* decomposition flask causes a greater displacement in the gas-measuring tube than the volume of added acid. This displacement is greater by about 3 to more than 5 cc., depending on the barometric pressure, the temperature, and the acid concentration, and is attributable to the vapor tension of the reagent-acid.

The volume reading of the evolved carbon dioxide, in the present Chittick method, consequently requires an empirical correction equal to the difference between the volume of reagent-acid used and the corresponding reading of the displacement effected in the gas-measuring tube after equalization of the internal and external pressures. This correction may vary during a working day. Subsequent to this correction the usual procedure of the method is followed.

Self-explanatory data from the determination of carbon dioxide in a self-rising flour are presented in Table I. A 5.10 gm. sample was used.

Sample portions of self-rising flour larger than 5.10 gm. somewhat diminish the error effected by vapor-pressure of the reagent-acid but do not eliminate the effect of this error upon the results. A 17.0-gm. sample portion requires 50 cc. instead of 15 cc. of reagent-acid, makes the procedure less satisfactory, and yields inaccurate results. Results using a 17.0-gm. sample portion are given in Table II.

TABLE I
SELF-RISING FLOUR (5.10 gm. sample)

	a *	b *	c *
Temperature, °C	20	20	24
Pressure, mm.	760	769	755
Reading, cc.	17.8	19.1	21.2
Reagent-acid vapor-pressure correction, cc.	-3.0	-4.3	-5.8
Reading (corrected), cc.	14.8	14.8	15.4
Reading per 1.7 gm. sample, cc.	4.9	4.9	5.1
Reading \times factor	5.16	5.23	5.23
Carbon dioxide, %	0.52	0.52	0.52
(Calculations omitting vapor-pressure correction)			
Reading, cc.	17.8	19.1	21.2
Reading per 1.7 gm. sample, cc.	5.9	6.4	7.1
Reading \times factor	6.21	6.82	7.28
Carbon dioxide, %	0.62	0.68	0.73
Error, %	0.10	0.16	0.21
Per cent error	19.2	30.8	40.4

* Determinations made on different days.

TABLE II
SELF-RISING FLOUR (17.0 gm. sample)

Temperature, °C.	22	22
Pressure, mm.	758	758
Reading, cc.	55.4	55.6
Reagent-acid vapor-pressure correction, cc.	-5.4	-5.4
Reading (corrected), cc.	50.0	50.2
Reading per 1.7 gm. sample, cc.	5.0	5.02
Reading \times factor	5.20	5.22
Carbon dioxide, %	0.52	0.52
(Calculations omitting vapor-pressure correction)		
Reading, cc.	55.4	55.6
Reading per 1.7 gm. sample, cc.	5.54	5.56
Reading \times factor	5.76	5.78
Carbon dioxide, %	0.58	0.58
Error, %	0.06	0.06
Per cent error	11.5	11.5

Data from the determination of carbon dioxide in a baking powder are exhibited in Table III.

Without due allowance for the above reagent-acid vapor-pressure correction, results for carbon dioxide in self-rising flour (using 5.1 gm. sample) are in serious error, and results for baking powder are in error in sufficient degree to require attention. The correction factor should be determined at least twice a day, and oftener with changing atmospheric conditions. This correction is of such importance as to demand observation by users of the Chittick method.

TABLE III
BAKING POWDER (1.70 gm. sample)

Temperature, °C.	22	22
Pressure, mm.	756	756
Reading, cc.	137.0	136.5
Reagent-acid vapor-pressure correction, cc.	-5.5	-5.5
Reading (corrected), cc.	131.5	131.0
Reading \times factor	135.0	134.4
Carbon dioxide, %	13.5	13.4
(Calculations omitting vapor-pressure correction)		
Reading, cc.	137.0	136.5
Reading \times factor	140.6	140.0
Carbon dioxide, %	14.1	14.0
Error, %	0.6	0.6
Per cent error	4.4	4.5

THE VISCOSITY OF FLOUR SUSPENSIONS

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(Received for publication August 10, 1928)

Replying to my notes on the theoretical interpretation of viscosity determinations of flour suspensions (1928) Denham, Watts, and Scott-Blair (1928) refer to their second paper on this subject (1927) in which, in their opinion, they have shown that the viscosity measurements underlying the above-mentioned theoretical discussions are free from systematic errors.

However, in connection with the investigations of Bungenberg de Jong (1923), cited in my first paper, I must continue to object to this point of view. This journal is not the right place to discuss problems of purely physical-chemical nature. Therefore I will restrict my remarks to some data given by Denham, Watts, and Scott-Blair (1927) to show the reliability of the viscosity measurements. These data are to be found in Tables II and III (Page 210). Apparently the viscometers used varied only in the bores of the capillaries. One would expect the velocity of flow in the different viscometers to be approximately proportional to the fourth power of the capillary bore (see page 207). For tubes No. 4 and No. 1 the relation of the velocities is 2.2, that for the fourth powers of the bores 167 (Table II). It is hard to

imagine that this lack of agreements disappears in investigating flour suspensions instead of water.

In the second place the viscosity numbers found for flour suspensions of the same concentration with different viscometers show variations of several per cents. The agreement may be entirely sufficient for most practical purposes, for testing theoretically deducted equations a greater accuracy is wanted.

For the rest I maintain my objections to the applications of the laws of liquids on the flow of flour suspensions, even of low concentration. To my opinion these objections alone are serious enough to exclude the introduction of Einstein's formula in this field of applied colloid chemistry at the present time.

Literature Cited

- Bungenberg de Jong, H. G.
1923 Viscosimetric researches on lyophilic sols. *Rec. Trav. Chim. des Pays-Bas* **42**: 1-24.
- Denham H. J., Scott-Blair G. W., and Watts G.
1927 Note on the use of Ostwald viscometers for flour suspensions. *Cereal Chem.* **4**: 206-221.
- Denham H. J., Watts G., and Scott-Blair G. W.
1928 Note on the measurement of viscosity in flour suspensions. *Cereal Chem.* **5**: 330.
- Scott Blair G. W., Watts G., and Denham H. J.
1927 Effect of concentration on viscosity of flour suspensions. *Cereal Chem.* **4**: 63-68.
- Van der Lee, G.
1928 The viscosity of flour suspensions. *Cereal Chem.* **5**: 10-13.

BOOK REVIEW

Die Bestimmung der Wasserstoffionenkonzentration von Flüssigkeiten. (The Determination of the Hydrogen Ion Concentration of Liquids.) By Ernst Mislowitzer. 378 pages, 184 illustrations. Price, cloth binding, RM 25.50. Julius Springer, Berlin, 1928.

This book will fill an important place in the literature on the determination of hydrogen ions, for it is devoted primarily to lucid and detailed discussions of technic. The need for such a work has become especially urgent in the last few years. Altho the literature on the subject has grown at an amazing rate, it has been unable to keep up with developments in technic, and none of the texts now available contain such an abundance of material on the actual carrying out of hydrogen ion measurements as does Dr. Mislowitzer's book.

The reader is assured in the foreword that the book is based on years of practical teaching experience, and that "all parts have been lived, not merely written—and assembled." The arrangement of the material is to be commended. The book opens with a concise treatment of general theoretical considerations. The mathematical relations involved are next taken up, prefaced by a brief discussion of the principles of differentiation and integration, for the benefit of those who have had no calculus or have forgotten how to use it.

The next two sections deal with the electrical units and the construction and operation of the principal electrical instruments employed in electrometric measurements. Here, as elsewhere in the book, the discussion of theory is limited but admirably well developed and easy to grasp. These sections should be especially useful to investigators wishing to experiment with other combinations of instruments than those provided in the usual potentiometer set-ups.

The two succeeding sections, comprising nearly a third of the book, describe the theory, construction, and manipulation of a wide variety of electrodes, including the quinhydrone, manganese, antimony, bimetallic, and glass electrodes, and give detailed instructions for their use in combination with the other apparatus requisite to electrometric measurements. The following section treats electro-titration, and the concluding section outlines the theory and practice of the most important colorimetric methods.

The bibliography will undoubtedly be of value, especially to students of biology and medicine. A commendable feature of this bibliography is that each item is accompanied by a marginal reference to an abstract in the "Berichte über die gesamte Physiologie und Pharmakologie." Another interesting feature of the book is the brief summary given at the beginning of each chapter.

It is hardly necessary to say that an English translation of this work would be highly desirable. The book is written in clear, uninvolved German, and should offer no great difficulties to anyone with a fair reading knowledge of scientific German.

The binding, printing, and illustrations are all of high quality. The book should constitute a valuable, if not indispensable, addition to the library of any chemist interested in measurements of this kind.

—Clinton L. Brooke.

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